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THE MANUFACTURE AND USE OF SELECTED ARYL AND ALKYL ARYL PHOSPHATE ESTERS

T. W. Lapp

Midwest Research Institute

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THE MANUFACTURE AND USE OF SELECTED ARYL AND ALKYL ARYL PHOSPHATE ESTERS

TASK I

FEBRUARY 1976

FINAL REPORT

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OFFICE OF TOXIC SUBSTANCES
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Eleven aryl and alkyl aryl phosphate esters were selected for investigation as potential environmental contaminants. Information was collected on the production quantities, manufacturers and their processes, users and their processes, and the environmental management of both the producers and users. Alternatives for selected organophosphate esters are considered.

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Cresyl diphenyl phosphate
Triphenyl phosphate
Dibutyl phenyl phosphate
Isopropylphenyl diphenyl phosphate
Octyl diphenyl phosphate
Methyl dipshenyl phosphate
Isodecyl diphenyl phosphate
Dimethyl xylyl phosphate
Xenyl diphenyl phosphate
p-Chlorophenyl diphenyl phosphate

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THE MANUFACTURE AND USE OF SELECTED ARYL AND ALKYL ARYL PHOSPHATE ESTERS

Task I

EPA Contract No. 68-01-2687

EPA Project Officer: Thomas Kopp

For

Environmental Protection Agency

Office of Toxic Substances
4th and M Streets, S.W.
Washington, D. C. 20460

February 1976

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REVIEW NOTICE

This report has been reviewed by the Office of Toxic Substances, EPA and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

PREFACE

This report presents the results of Task I of a project entitled "Study on Chemical Substances from Information Concerning the Manufacturing, Distribution, Uses, Disposal, Alternatives, and Magnitude of Exposure to the Environment and Man." Task I, "The Manufacture and Use of Selected Aryl and Alkyl Aryl Phosphate Esters," was performed by Midwest Research Institute (MRI) under Contract No. 68-01-1687 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. This program had MRI Project No. 3955-C.

Task I was conducted from 1 September 1974 to 14 March 1975 by Dr. T. W. Lapp, Associate Chemist, who served as project leader and prepared this report, under the supervision of Dr. E. W. Lawless, Head, Technology Assessment Section. Dr. I. C. Smith, Senior Advisor for Environmental Science provided technical assistance and supervision.

MRI would like to express its sincere appreciation to the various companies who provided technical information for this report and especially to Mr. Paul Levesque, FMC Corporation, for his valuable assistance in this subject area.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon, Assistant Director
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5 February 1976

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SECTION 1

INTRODUCTION

Organophosphate esters find widespread usage in numerous consumer-oriented and industrial products where fire retardancy is a desirable property or a mandatory requirement. In addition to the halogens, phosphorus is one of the most effective elements in combating the propagation of fire, and incorporation of phosphorus into organic compounds, via organophosphate esters, has led to its widespread usage for that purpose. In very general terms, organophosphate esters are used as plasticizers in poly(vinyl chloride) plastic materials and in industrial hydraulic fluids. Because of their use in poly(vinyl chloride), as a flame retardant, they are found in numerous consumer products, such as automobile and household goods, and in industries having wide geographical coverage, such as the construction industry. The use of these esters as fire resistant hydraulic fluids leads to a widespread utility in industries operating hydraulic systems in the immediate vicinity of high temperature sources.

The primary objectives of this study are to collect information on the production quantities, manufacturers and their processes, users and their processes, and the environmental management of both the producers and users. This information is organized into a format which will assist the government agencies in the evaluation of any regulatory alternatives for these materials. The goal of Task I of the study has been to assist the EPA in the evaluation of the potential for environmental contamination by selected organophosphate esters.

Eleven aryl and alkyl aryl phosphate esters were selected for investigation as potential environmental contaminants. These were:

* Tricresyl phosphate
* Cresyl diphenyl phosphate
* Triphenyl phosphate
* Dibutyl phenyl phosphate
* Isopropylphenyl diphenyl phosphate
* Octyl diphenyl phosphate (2-ethylhexyl diphenyl phosphate)
* Methyl diphenyl phosphate
* Isodecyl diphenyl phosphate
* Dimethyl xylyl phosphate
* Xenyl diphenyl phosphate
* p-Chlorophenyl diphenyl phosphate

Throughout the literature and in discussions with personnel directly involved with the industry, two different terminologies--with respect to phosphate esters is widespread. In the hydraulics industry, fluids that resist flame propagation are termed fire resistant fluids whereas in the field of plasticizers, phosphate esters are termed fire retardant plasticizers. In this report, the term fire resistant will be applied to discussions involving their use in hydraulic fluids and fire retardant when discussing plasticizers. While this method is rather inconsistent, it is the accepted terminology within the respective industries.

SECTION II

SUMMARY

For the time period 1964 to 1973, approximately 847 million pounds of phosphate esters were produced, of which tricresyl phosphate accounted for about 396 million pounds. The other phosphate esters studied and their respective approximate production figures, in million pounds, were isopropylphenyl diphenyl (46), cresyl diphenyl (167), triphenyl (96), dibutyl phenyl (24), methyl diphenyl (37), 2-ethylhexyl diphenyl (58) and isodecyl diphenyl (23). Nearly all of the production of these esters is utilized in the United States with only approximately 2 to 3% being exported.

Essentially all of these esters are produced commercially by the reaction of the appropriate alcohol or phenol with phosphoryl chloride. Reaction conditions vary somewhat depending upon whether the triaryl or alkyl aryl phosphate esters are being produced. Currently, the five companies who produce these triaryl or alkyl aryl phosphate esters are FMC Corporation, Monsanto Industrial Chemicals Company, Stauffer Chemical Company, Sobin Chemical Company, and Eastman Kodak Company. Of these, the first three are the major producers with the latter two producing relatively small quantities of selected esters.

The major areas of utilization of these esters are as fire retardant plasticizers (resin modifiers) and fire resistant hydraulic fluids. These two areas presently account for approximately 90% of the total use of these esters. During the 10-year period from 1964 to 1973, the major use of two of these esters, cresyl diphenyl and methyl diphenyl, was as gasoline additives for ignition control but this area has been inactive since about 1971. Most of these phosphate esters are utilized in both of the major use areas, however, some have singular uses in either one area or the other. Dibutyl phenyl phosphate is used solely as an aircraft hydraulic fluid and trixylenyl phosphate is utilized almost exclusively in the formation of industrial hydraulic fluids. Methyl diphenyl phosphate is no longer produced on a commercial basis. Triphenyl phosphate finds almost sole utilization as a plasticizer in cellulosic and polyphenylene oxide materials.

During the middle 1960's, the predominant areas of utilization of these esters were as fire retardant plasticizers and gasoline additives. In more recent years, their use as gasoline additives has ceased and their utility in fire resistant hydraulic fluids has increased dramatically. Hydraulic fluid usage represents the largest contributor of these esters into the environment. It is estimated that approximately 80% of the annual "consumption" of hydraulic fluids occurs through leakage in the hydraulic systems.

According to most observers directly related to this industry, the overall future growth of both the plasticizer and hydraulic fluid fields is expected to be in the range of 8 to 10%/year. Since these two areas constitute the major use of these phosphate esters, it appears that future growth in production should also approximate this 8 to 10% figure in future years.

SECTION III

HISTORICAL DEVELOPMENT AND FUTURE OUTLOOK

The historical development of selected aryl and alkyl aryl phosphate esters as plasticizers, hydraulic fluids, and additives is reviewed. Their future outlook, from 1974 to 1984, is discussed from a generalized viewpoint.

HISTORICAL DEVELOPMENT

Triaryl phosphate esters were first reported in the literature over 100 years ago and the utility of these esters as plasticizers for cellulosics was initiated about the turn of the century. The preparation of triphenyl phosphate was first reported in 1854[1] but remained little more than another research chemical until 1910 when a patent was issued to the Celluloid Company of New York[2] for its use with cellulose acetate to produce a "celluloid-like" material. It was hoped that this process would overcome the dangers of flammability of celluloid by (a) using the acetate instead of the nitrate and (b) plasticizing with tripheny' phosphate for reinforcement and its nonburning properties. Shortly thereafter, in 1913, Klatte in his pioneering patent demonstrated that useful and processible forms of poly(vinyl chloride) could be obtained when he employed triphenyl phosphate as a plasticizer. In 1922 Laska and Brillwitz[3] were issued patents for the production of tricresyl phosphate and cresyl diphenyl phosphate and in 1923 a patent was issued to St. John[4] for the production of cresyl diphenyl phosphate. In this same time period triphenyl phosphate and tricresyl phosphate began to find usage in plastics and lacquers.[5] In 1929 the Celluloid Corporation patented a mixture comprising vinyl compounds and aryl phosphates, including tricresyl phosphate. Surprisingly, vinyl chloride was not mentioned as one of the vinyl compounds.[2] However, in the following year a patent was issued to Du Pont for a coating composition using tricresyl phosphate as a possible softener. By 1933 developmental quantities of poly(vinyl chloride) had been introduced in a variety of product forms in the U.S. and Germany and both tricresyl phosphate and dibutyl phthalate, patented in 1920 by H. T. Clarke, were the recognized plasticizers.[6]

The discovery in 1933 by Dr. W. L. Semon, of B. F. Goodrich, that poly(vinyl chloride) could be plasticized with high boiling esters, including tricresyl phosphate, without the use of a lower boiling solvent is considered to be one of the most important contributions to the development of poly(vinyl chloride) as well as to the plasticizer industry.[7] During the decade 1930 to 1940 there was a growing interest and activity in the field of plasticizers and plasticized compounds but it did not compare with the magnitude of research in subsequent years.

The development of the hypoid gear for use in automobile rear axles by the Gleason Works in 1925 provided the impetus for further developmental work in the area of gear lubricants. Those gear lubricants, which had previously proved quite satisfactory for spur and bevel gears, were inadequate for hypoid gears. General usage of this type of gear was delayed until a suitable class of extreme-pressure (EP) lubricants was available.

By 1937 practically the entire production of automobiles in this country and a large percentage of the trucks were using hypoid rear axles. The increased developmental activity for extreme-pressure (EP) lubricants led to the introduction of triaryl phosphate esters as EP agents.

During the war years and those immediately subsequent, the interest in plastics, particularily poly(vinyl chloride), mushroomed and thousands of compounds, many chosen empirically, were tested and evaluated for the many new applications that appeared after the war. In 1941 the production of tricresyl phosphate was less than 10 million pounds[8] but increased rapidly to over 20 million pounds in 1943 to 1944 before falling back to about 10 million pounds after the war.

As in the case with plasticizers, the emphasis on developmental research provided by World War II led to a broadening of the areas of application for EP agents, including tricresyl phosphate. It was during this time period that the use of phosphate esters first appeared as fire resistant hydraulic fluids for the military in aircraft hydraulic systems and in launching catapults on aircraft carriers. After World War II the usage of triaryl phosphate esters, predominantly tricresyl phosphate and cresyl diphenyl phosphate, began a slow, gradual increase until the latter 1960's.

In the years immediately following World War II, synthetic fluids were applied to industrial hydraulic systems. By the early 1950's, water-glycol fluids were developed as low-cost substitutes for the synthetic fluids and in the latter 1950's, water-in-oil emulsions were introduced into the market.

In 1950, the production of tricresyl phosphate was over 15 million pounds and triphenyl phosphate was over 6 million pounds. The early 1950's saw not only an increased interest as plasticizers, but the advent of phosphate esters as gasoline additives. New alkyl aryl phosphate esters appeared on the scene, such as 2-ethylhexyl diphenyl phosphate, dimethyl phenyl phosphate, and methyl diphenyl phosphate. The latter two found usage as gasoline additives as did cresyl diphenyl phosphate and tricresyl phosphate. In 1953, Shell Oil Company commercially introduced tricresyl phosphate as an additive for automobile fuels to control sparkplug fouling and preignition.

During the 1950's the utilization of synthetic hydraulic fluids decreased sh rply, evidently due at least in part to being oversold, and fell from favor with many hydraulic fluid users. In 1960, fire resistant fluids probably accounted for about 2 to 3% of the total hydraulic fluid consumption. By 1964, fire resistant fluids had risen to only approximately 6% of the total fluid consumption, with phosphate esters accounting for only about 10% of the total fire resistant fluids being used.

In general, from the mid-1950's to 1964, the major use areas of aryl and alkyl aryl phosphate esters were as plasticizers, gasoline additives, lubricant additives, and functional fluids.

FUTURE OUTLOOK

The future use of the aryl and alkyl aryl phosphate esters, except for tricresyl phosphate and cresyl diphenyl phosphate, appears to be increasing at the present time. Usage as fire retardant plasticizers and in fire resistant hydraulic fluids accounts for approximately 80 to 90% of the annual consumption of these phosphate esters. The manufacturers of these esters are predicting an average overall growth rate in both of these fields of 8 to 10%/year for 1976 and further into the future. Due to the present economic climate, use in the major areas fell from 1973 levels but should recover during 1975.

One of the overriding factors in all discussions with both producers and users of these esters was the increase in cost, both in terms of raw materials and the finished product. For producers, the shortages in the supply of raw materials and their rapidly increasing cost are of greatest concern since these costs are, in turn, passed on to the users.

Tricresyl phosphate and cresyl diphenyl phosphate should both show declines in production during the next decade. Monsanto Industrial Chemicals Company ceased the commercial sale of tricresyl phosphate in 1974 and reportedly will do the same with cresyl diphenyl phosphate in 1975.

The reasons for this discontinuation were basically due to the shortage of cresylic acid, increased costs, and their inability to control the ortho isomer content. This decrease in production will, of course, create further pressure on the supply of these two chemicals. However, it should be noted that in view of the methods of production of triaryl esters, production of either or both of these materials could commence on very short notice.

Phosphate esters which find rather general utilization throughout both of the major use areas are expected to increase in production at a rate consistent with the increases for the two areas. Certain specialty items, such as triphenyl phosphate, will probably not experience an average annual growth as high as the more general use esters.

Overall, the production and consumption of these phosphate esters should be in the range of 8 to 10%/year for the next decade, assuming that the current economic situation is clarified. The production of tricresyl phosphate, however, is expected to decline rather sharply over the next few years. Cresyl diphenyl phosphate will decline but probably not as sharply as will tricresyl phosphate. Future legislation regarding flammability requirements could alter the overall growth rate of phosphate esters significantly. Likewise, the introduction of new products will obviously affect the projected growth rate of specific materials.

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SECTION IV

MARKET INPUT-OUTPUT DATA

Cumulative data are presented for the selected phosphate esters during the time period 1964-1973. The data are considered in terms of production, importation, exportation, use patterns, and final products of these esters.

PRODUCTION

The total production quantities of each of the phosphate esters included in this study on an annual basis and for the 10-year time span (1964 to 1973) are shown in Table 1. In the United States, the three major producers of aryl and alkyl aryl phosphate esters are FMC Corporation, Stauffer Chemical Company, and Monsanto Industrial Chemicals Company. Sobin Chemicals, Inc. (Montrose Chemicals Division), and Eastman Kodak Company produce smaller quantities of selected aryl phosphate esters. In terms of total production over the 10-year span, the three major phosphate esters are tricresyl phosphate, cresyl diphenyl phosphate, and triphenyl phosphate.

As shown in Table 1, the total quantity of phosphate esters produced during the 10-year span was approximately 847 million pounds. This does not include any production data for either dimethyl xylyl phosphate or mono-o-xenyl diphenyl phosphate. For the first material, no information could be located concerning any production figures and only two references to any possible utility with no information being available on current or past actual usage. In the case of the latter material, the company who reportedly produced the material stated that they had never made any phosphate esters. The data reported in this table show some variance with the figures reported in the U.S. International Trade Commission Reports on Synthetic Organic Chemicals. It is believed that some, but not all, of the production figures for the proprietary mixed alkyl aryl esters manufactured by Monsanto Industrial Chemicals Company are included in the U.S. International Trade Commission Reports. Since the actual quantities of this material are unknown to Midwest Research Institute, no consideration has been given to this material in the tabulation and thus, certain discrepancies will occur in a comparison of the total figures.

Table 1. ANNUAL PRODUCTION OF VARIOUS PHOSPHATE ESTERS
(x 10^6 lb/year)

Year	TCP	IPDP[b/]	CDP	TPP	DBPP	MDPP	ODPP	IDPP	CPDP	Total[a/]
1964	32.4	--	16.1	9.0	(1.6)	(4.8)	(9)	--	--	72.9
1965	34.8	--	19.7	(8.9)	(1.8)	5.8	(9)	--	--	80.0
1966	39.8	--	20.0	8.8	(2.0)	(5.8)	(8)	--	--	84.4
1967	42.9	--	18.2	8.7	(2.4)	(5.9)	(8)	--	--	86.1
1968	44.3	--	19.8	7.9	(2.8)	(5.9)	(5)	(1)	$\ll$ 0.1	86.8
1969	(43.5)	(3)	11.1	9.2	(2.3)	6.0	(4)	(1.5)	$\ll$ 0.1	80.7
1970	(41.0)	(5)	12.7	10.6	(2.5)	(2)	(4)	(4)	--	81.8
1971	(40.8)	(8)	20.4	(10)	(2.7)	(1)	(3)	(4.5)	--	90.4
1972	(38.2)	(12)	14.6	(11)	(2.9)	--	(3)	(5)	--	86.7
1973	(37.8)	(18)	14.2	(12)	(3.1)	--	(5)	(7)	--	97.1
Total	(395.5)	(46)	166.8	96.1	(24.1)	(37.2)	(58)	(23)	$\ll$ 0.2	(846.9)

( ) MRI estimates based on discussions with manufacturers

Abbreviations: TCP = tricresyl phosphate
IPDP = isopropylphenyl diphenyl phosphate
CDP = cresyl diphenyl phosphate
TPP = triphenyl phosphate
DBPP = dibutyl phenyl phosphate
MCPP = methyl diphenyl phosphate
ODPP = octyl diphenyl phosphate (2-ethylhexyl diphenyl phosphate)
IDPP = isodecyl diphenyl phosphate
CPDP = p-chlorophenyl diphenyl phosphate

a/ Some of the total figures will vary somewhat with the total figures reported in the U.S. International Trade Commission Reports on Synthetic Organic Chemicals. It is felt that a portion of the proprietary alkyl aryl phosphate ester mixture produced by Monsanto is included in the Commission Reports but is excluded from these totals.

b/ Throughout this report, this name will be utilized in all discussions and tables. Although this name is the specific compound that is closest to the actual product, the different grades represent different ratios of isopropylphenols to phenol and the term "mixed isopropylphenyl phenyl phosphate" is a more accurate representation.

Future production of the phosphate esters is expected to follow the predicted growth for the use areas of fire retardant plasticizers and fire resistant hydraulic fluids. After a period of relatively zero growth during 1974 and 1975, each of these areas should attain an annual growth of 8 to 10%/year. Since these two areas represent the largest use of the phosphate esters, it would be expected that production would increase at approximately the same rate. Barring any further economic recessions, this would indicate an annual production of 185 to 215 million pounds per year by 1984 as shown in Figure 1.

IMPORTATION

Importation of phosphate esters over the 10 years from 1964 to 1973 have generally been negligible in relation to the total quantities of aryl and alkyl aryl phosphate esters produced in the United States. A U.S. International Trade Commission annual report[1/] lists the following materials as having been imported.

Material	Quantity imported (pounds) 1973	1974	1971	1970	1969	1968
Trixylenyl phosphate plus butyl benzyl phthalate	-	70,636	-	-	-	-
Cresyl diphenyl phosphate	-	-	3,000	-	-	-
Phosphate esters	-	-	43,726	-	-	-
Tricresyl phosphate	-	-	-	1,565	-	-

The originating country for these imports was not specified but it is very probable that it was the United Kingdom. As shown in the listing, the quantities are extremely small. Phosphate ester manufacturers indicate that phosphate esters are imported in greater quantities than shown in the above listing but, overall, comprise less than 1% of the total quantity of esters produced on an annual basis and should continue at approximately that level for the next 10 years.

EXPORTATION

From the detailed use patterns shown in the next subsection, the quantities of phosphate esters being exported comprise approximately 3% of the total production. An appreciable percentage of the exports are shipped to Canada for use by pipeline companies in gas pumping

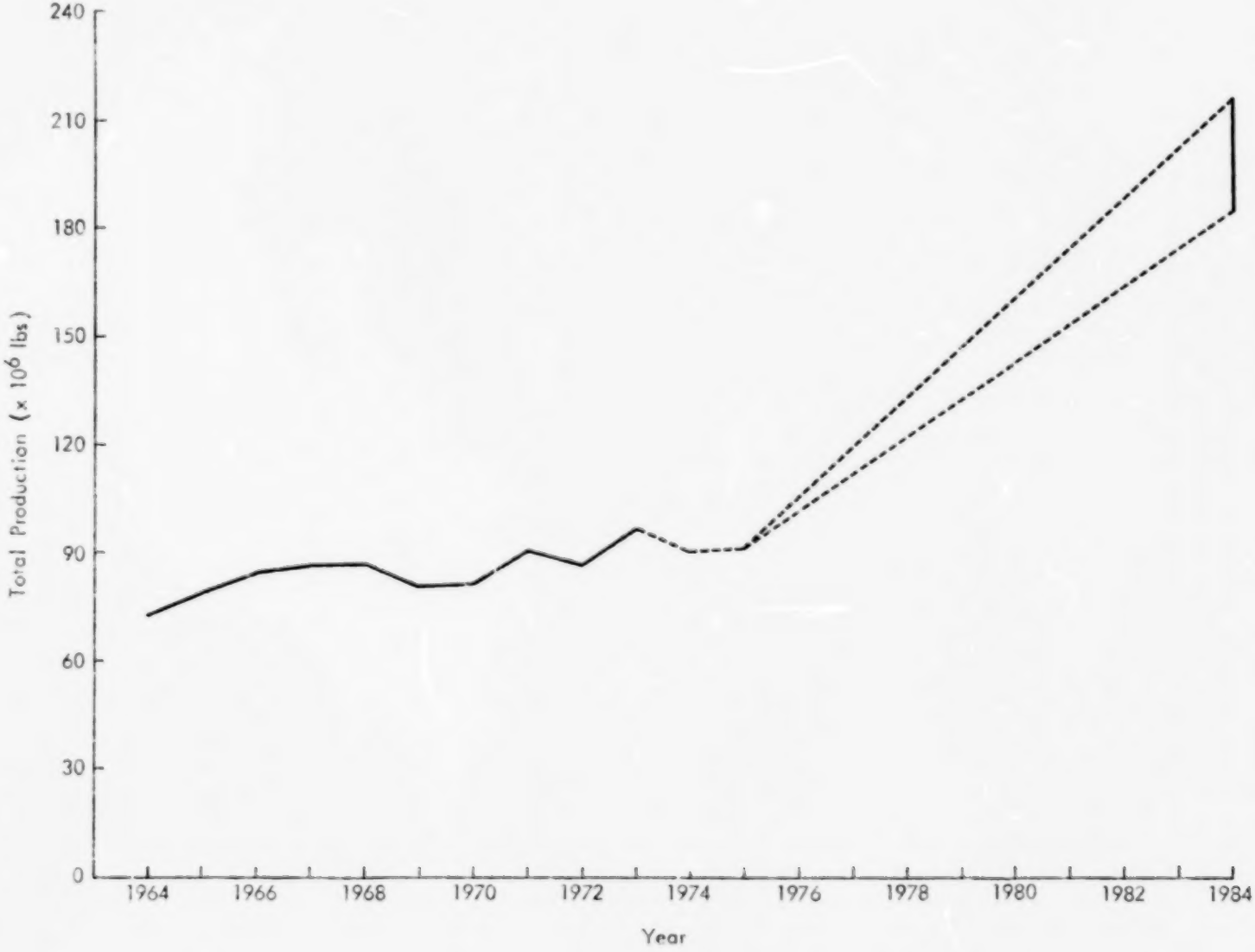

Figure 1. Estimated total production and future growth of phosphate esters.

systems in remote areas. Other areas importing phosphate esters from the United States include Mexico, Japan, United Kingdom and some European countries. The quantities of phosphate esters exported has remained basically constant at about 3% or less of the total production for the last 10 years and should remain at approximately that level for the next 10 years.

USE PATTERNS

The five basic areas of utilization of the phosphate esters are shown in Table 2 in terms of the estimated annual consumption for each area and the percentage contribution of each area towards the total for the respective year. As shown, the area of plasticizers has consistently been the primary use, although recently the combined areas of hydraulic fluids and lubricant additives are approximately the same as that for plasticizers. Within the general area of plasticizers, several other use areas are included which have a direct relationship to the plastics or rubber industry. These areas include pigment dispersants, peroxide carriers, adhesives, and rubber plasticizers. Aircraft hydraulic fluids are included in the general classification of hydraulic fluids. The category of exports and miscellaneous includes, in addition to exportation, the areas of air filter media, lacquer coatings, and wood preservatives.

A more detailed use pattern is shown below for the years 1970, 1972, and 1973 for three phosphate esters: tricresyl phosphate, cresyl diphenyl phosphate, and isopropylphenyl diphenyl phosphate. Triphenyl phosphate, dibutyl phenyl phosphate, isodecyl diphenyl phosphate, and octyl diphenyl phosphate have basically singular uses.

	Approximate percent utilization of TCP, cresyl diphenyl phosphate and isopropylphenyl diphenyl phosphate		
Use area	1973	1972	1970
Hydraulic fluids	43	43	39
Lubricant additive	11	11	11
Plasticizer (PVC)	25	25	25
Air filter media	5	5	4
Rubber plasticizer	4	4	4
Coatings	2	2	2
Pigment dispersant	2	2	1
Adhesive, wood treatment, and peroxide carrier	2	2	3
Gasoline additive	-	-	4
Export	3	3	4
Miscellaneous	3	3	3

Table 2. ESTIMATED ANNUAL CONSUMPTION AND PERCENTAGE COMPOSITION BY USE AREA
(quantities x 10^6 lb/year)

Year	Plasticizer		Hydraulic fluid		Lubricant additive		Gasoline additive		Export and miscellaneous	
	Quantity	%	Quantity	%	Quantity	%	Quantity	%	Quantity	%
1964	37.1	50.9	11.6	15.9	4.0	5.5	17.7	24.3	2.5	3.4
1965	39.3	49.1	15.3	19.1	4.2	5.3	18.7	23.4	2.5	3.1
1966	41.9	49.6	17.3	20.5	4.4	5.2	18.2	21.6	2.6	3.1
1967	41.3	48.0	18.9	22.0	4.6	5.3	17.7	20.6	3.6	4.1
1968	40.0	46.1	20.5	23.6	4.8	5.5	16.9	19.5	4.6	5.3
1969	33.4	41.4	21.3	26.4	5.3	6.6	16.0	19.8	4.7	5.8
1970	41.1	50.2	23.0	28.1	5.8	7.1	5.0	6.1	6.9	8.6
1971	49.8	55.1	24.7	27.3	6.4	7.1	2.5	2.8	7.0	7.7
1972	40.7	46.9	31.9	36.8	7.0	8.1	-	-	7.1	8.2
1973	41.8	43.1	40.1	41.3	7.7	7.9	-	-	7.5	7.7
Total	406.4	48.0	224.6	26.5	54.2	6.4	112.7	13.3	49.0	5.8

The three phosphate esters to which this listing is applicable comprise approximately 65 to 75% of the total production of the phosphate esters in this study. As shown above, the percentage utilization has not changed appreciably over the last 4 years. This detailed compilation also indicates the approximate utilization in several of the minor use areas.

Both the areas of fire retardant plasticizers and fire resistant hydraulic fluid are anticipated to show an annual rate of growth of approximately 8 to 10% after 1976. During the period from 1974 to 1976, it would be expected that both of these areas would show zero growth rate or perhaps some decline in consumption. Assuming an 8 to 10% annual growth rate, it could be expected that in 1984, the area of fire retardant plasticizers would utilize 82 to 98 million pounds per year and the area of fire resistant hydraulic fluids would consume an additional 76 to 91 million pounds per year. The relatively minor use areas of lubricant additives and miscellaneous uses are expected to approximately double their consumption of these phosphate esters by 1984. All of these projected figures assume that no severe economic recessions occur during the time period 1976 to 1984.

FINAL PRODUCTS

Currently, the ultimate uses of the phosphate esters in this study are predominantly in plastic materials and hydraulic fluids (including lubricant additives). In the plastics industry, about 90% of all the esters used as plasticizers, except triphenyl phosphate, are used in poly(vinyl chloride). Triphenyl phosphate is used in cellulosics and modified polyphenylene oxide (Noryl) resins with cellulosics accounting for approximately 60% of its total in 1973.

The major consumer products for phosphate ester plasticized poly(vinyl chloride) are in automotive and truck interiors, as vinyl-coated fabric upholstery, vinyl film upholstery and dashboard coverings; wire and cable coatings and insulation; wall coverings; and the construction industry. In 1965, the major use areas for poly(vinyl chloride) were in the construction and housing markets. Phosphate esters were used as plasticizers where flame retardancy was a requirement such as in light diffusers, wall coverings and flexible doors. These esters are still used for such purposes at the current time but the automotive market has been the major growth area from 1964 to 1973.

Prior to 1966, triphenyl phosphate was used almost exclusively in cellulosics; however, since the introduction of Noryl, its application as a plasticizer for this engineering plastic has been increasing steadily and now constitutes approximately 40% of its utilization. Cellulosics are used primarily in packaging; home applications such as photo albums, handles on small tools, box lids for greeting cards and stationary; and

safety face shields. During the time period 1964 to 1973, the quantity used in the area of packaging decreased somewhat and the market for safety face shields increased. The use of cellulosics in automobiles has almost been entirely replaced by other plastics.

Noryl is an engineering thermoplastic and finds utility in areas such as molded casings for home appliances, instruments, hand calculators, business machines and others; subway windows; windows in radar ovens; and electrical fixtures.

During the past 10 years the use of fire resistant hydraulic fluids has been the fastest growing area, in terms of percentage increase, for phosphate esters. The areas of utilization have basically remained the same, except for the area of gas turbines. Use of phosphate esters in control systems and gas turbines in remote areas is an area of increasing growth.

Industrial uses of fire resistant hydraulic fluids are found in the basic metals industry, automotive industry in die casting equipment and foundries, steel industry, and other industries using hydraulic fluids where high temperature could pose a fire hazard if the hydraulic system developed leakage.

REFERENCES TO SECTION IV

1. U.S. International Trade Commission, "Imports of Benzenoid Chemicals and Products," Annual Reports 1968-1972.

SECTION V

GENERAL MANUFACTURING PROCESS

Five companies currently produce the aryl or alkyl aryl phosphate esters under consideration in this study: Monsanto Industrial Chemicals Company; FMC Corporation, Industrial Chemicals Division; Eastman Kodak Company; Sobin Chemicals Inc. (Montrose Chemical Division); and Stauffer Chemical Company, Specialty Chemical Division. Further information regarding the different esters manufactured by each company, production sites, capacities, and yearly production can be found in Section VI.

TRIARYL PHOSPHATE ESTERS

Many methods are available for the preparation of triaryl phosphate esters.[1/] However, the universal manufacturing process presently in use consists of the condensation of the aryl compound with phosphoryl chloride in the presence of a metal chloride catalyst as exemplified in Eq. (V-1).[2,3/]

$$3\ ArOH + POCl_3 \xrightarrow{catalyst} (ArO)_3PO + 3\ HCl \qquad (V\text{-}1)$$

Production is normally by the batch process although manufacturers are striving to convert the system to a continuous process and have accomplished this in many phases of the operation. Aluminum chloride or zinc chloride is commonly used as the catalyst at production sites in the United States. A generalized flowsheet of the manufacturing process is shown in Figure 2 and the material balance in Table 3. All of the current manufacturers employ multipurpose plants designed to produce all of the triaryl or alkyl aryl phosphate esters marketed by that company. The plants are not normally designed so that production can be interchanged between triaryl and alkyl aryl phosphate esters.

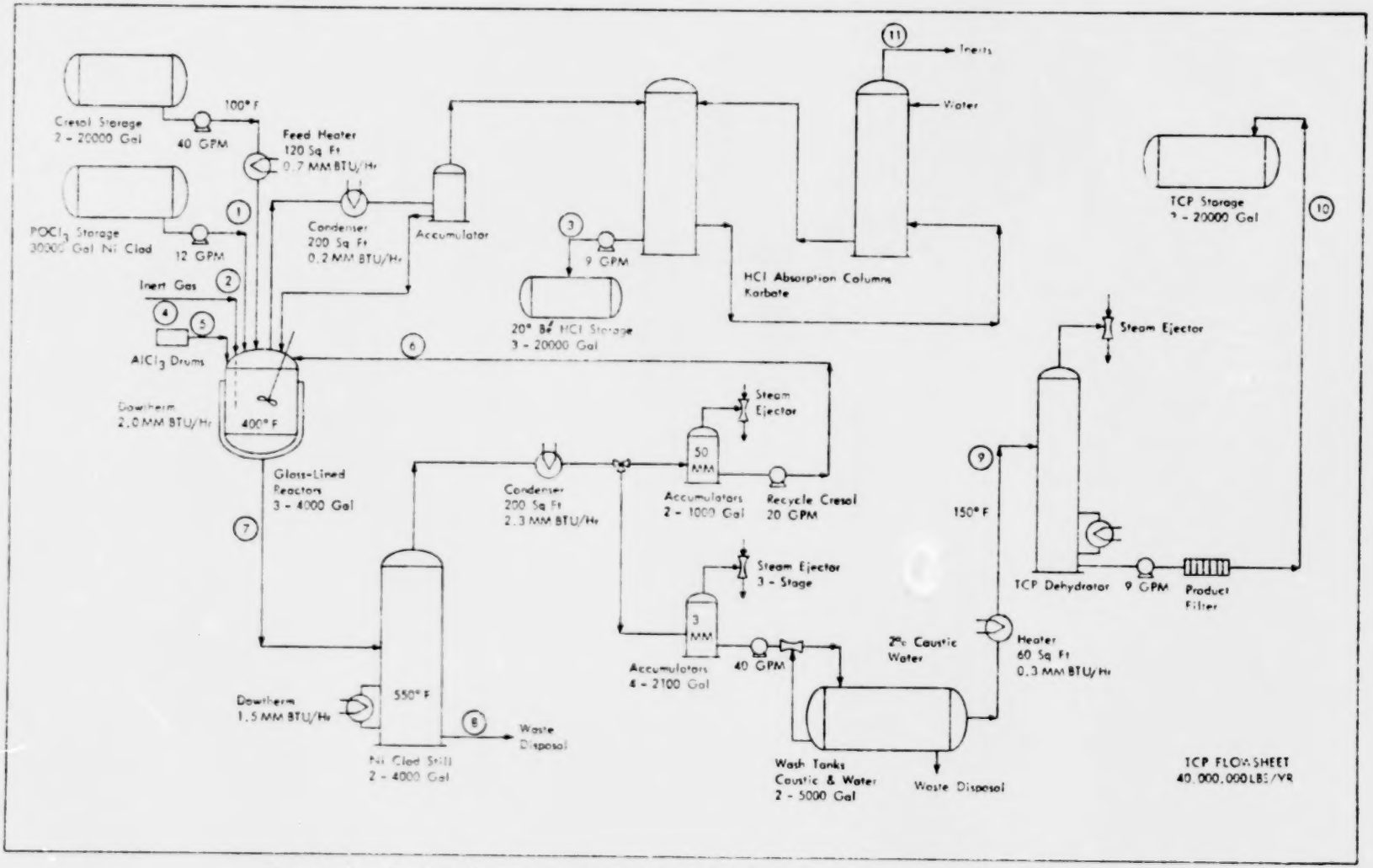

Figure 2. Production and waste flow diagram for tricresyl phosphate.

Table 3. MATERIAL BALANCE[a/]

Component	Stream number on Figure 2										
	1	2	3	4	5	6	7	8	9	10	11
Cresylic acid	5,053					600	600				
$POCl_3$		2,389									
$AlCl_3$					50		50	50			
HCl			1,500								
CO_2				14							14
Tricresyl phosphate							5,072	22	5,050	5,050	
Sludge[b/]							870	870			

a/ Figures are pounds per hour for the stream number as shown in Figure 2. If the plant operates 24 hr/day, 330 days/year, the tricresyl phosphate production will be 40×10^6 lb/year. The material balance is based on continuous flow for all streams, but in actual plant operation some streams will not be continuous flow.

b/ Sludge refers to the still residue and is composed of spent catalyst (aluminum cresylates, etc.) tars, and other ill-defined materials.

c: Similar figures for most of the other esters and the energy consumption for their production can be found in Section VI under the respective phosphate ester.

Overall reaction yield is 88% based on cresylic acid input.

As shown in the schematic diagram (Figure 2), the reactor is charged with a mixture of phosphoryl chloride, aluminum chloride (catalyst) and phenolic material. For triaryl phosphate esters in which the three aryl groups are the same, a slight excess of the phenolic material is employed to favor complete esterification. In reactions involving mixed phenolic materials (e.g., phenol and cresylic acid), the materials are added in stoichiometric quantities. The temperature is slowly raised to approximately 400° F over a period of about 8 hr. During the last hour of the reaction, the reactor vessel is flushed with an inert gas (N_2 or CO_2) to strip any remaining hydrogen chloride by-product. Because of the liberation of hydrogen chloride during the reaction, corrosion is a serious problem and glass-lined reactors are normally employed to circumvent this potential problem. To prevent excessive loss of reaction materials in the inert gas stream, the reactor is equipped with a reflux condenser where the phosphoryl chloride and phenolic material are condensed and returned to the reaction mixture.

The by-product hydrogen chloride effluent is passed through scrubbers to recover the hydrogen chloride and remove any organic material which passed through the reflux condenser. The hydrogen chloride is absorbed by a solution of HCl in the first scrubber and fresh water in the second scrubber. The scrubbers are constructed of Karbate to resist the corrosion of hydrochloric acid. The by-product hydrochloric acid is then either sold, retained for captive use within the company, or disposed in the waste treatment system. The by-product hydrochloric acid will contain traces of phenolic material.

After the reaction has progressed to completion, the contents of the reactor are transferred to a nickel-clad still and the unreacted cresylic acid is distilled under reduced pressure (50 mm). The pressure is then reduced to 3 mm to permit distillation of the tricresyl phosphate. Unreacted cresylic acid is returned for further processing.

The steam from the ejector normally contains some quantities of phenolic materials which have passed through the condenser during the course of the distillation of the phosphate ester. This steam is condensed and the resulting liquid, along with the phenolic material, is treated as liquid waste. After the distillation has been completed, the still pot contains a mixture of aluminum chloride, spent catalyst (aluminum phenolates or cresylates), and possibly some polymeric materials. These are removed and treated as solid waste.

The distilled phosphate ester is normally washed with a dilute (2%) solution of sodium hydroxide or treated with a solid material to neutralize and remove any hydrogen chloride, unreacted phenolic starting material, or partial esterification products which may have passed through the distillation process. After neutralization, the aqueous solution (or solid neutralizer) is separated and treated as a liquid (or solid) waste.

The phosphate ester is then pumped to a second water wash tank, dehydrated by heating under reduced pressure, treated with charcoal (e.g., NuChar) to remove traces of impurities and improve the color of the ester, and finally treated with a filtering aid (e.g., Filteraide). After filtration, the finished phosphate ester is removed to storage tanks for processing for shipment.

For triphenyl phosphate, the same procedures are used for the production and purification except that processing temperatures above 50° C are required to prevent solidification and zinc chloride is used as the catalyst. The finished triphenyl phosphate is sold in flaked form.

ALKYL ARYL PHOSPHATE ESTERS

In the manufacture of alkyl aryl phosphate esters, the same description as for the preparation and processing of the triaryl esters is applicable except for certain modifications of reaction conditions. For these esters, the phenolic material is added in stoichiometric quantities to the phosphoryl chloride to form an aryl or diaryl phosphoryl chloride. The reaction mixture is then cooled to below room temperature and the alcohol is added in slight excess of stoichiometric quantities. The hydrogen chloride by-product is removed under reduced pressure to avoid cleavage of the ester groups. Purification processes are basically the same as for the triaryl phosphate esters.

MANUFACTURING COSTS

The various cost factors related to the production of phosphate esters is delineated in this subsection for a simulated facility as shown in Figure 2. For the purposes of calculating these costs, the facility, as shown, will have a production capacity of 40 million pounds of tricresyl phosphate (TCP) per year and would operate 24 hr/day, 330 days/year.

Utility Costs

	Annual	Cents/Lb TCP
Steam at $2.00/1,000 lb	$41,976	0.105
Gas at $1.00/1,000 cu ft	39,600	0.099
Electricity at 2¢/kw-hr	24,552	0.061

Raw Material Costs

Raw material costs have been computed using the following current prices:

Cresylic acid	44¢/lb
$POCl_3$	34¢/lb
$AlCl_3$	20¢/lb
Carbon dioxide	6-1/4¢/lb

The annual costs are:

	Annual	Cents/Lb TCP
Cresylic acid	$17,608,694	44.022
$POCl_3$	6,433,099	16.083
$AlCl_3$	79,992	0.200
Carbon dioxide	7,000	0.018
Caustic	1,500	0.004
		60.327

Labor Costs

The necessary personnel required to operate a plant of this capacity have been estimated as follows:

10 operators at $50/day	$500.00/day
1 chemist at $70/day	70.00/day

Total annual labor costs, including a plant manager, secretary and office clerk are $263,400 or 0.658¢/lb/TCP.

Waste Disposal Costs

Three streams require waste treatment. Since the plant investment does not include treatment facilities, costs have been estimated on a service-by-others basis:

	Annual	Cents/Lb TCP
Aluminum chloride sludge at $20/drum	$158,400	0.396
Ejector water	1,188	0.003
Wash water	11,800	0.030
		0.429

Fixed Costs

In arriving at the cost of the plant, it is assumed that steam facilities would be present. It is, however, necessary to install a Dowtherm boiler to provide heat for the glass-lined reactors and nickel-clad stills. Plant investment includes the cost of major equipment, plus its installation and the necessary process piping, electrical and instrumentation for a completed plant. A building to house the reactors and most of the equipment with the exception of storage tanks is also included in the plant investment. The total plant investment, based on today's construction costs, is $2,957,000 exclusive of the cost of the plant site.

If the plant site is valued at $125,000, total investment will be $3,082,000. Based on amortization over 10 years, and using an interest rate of 12%, the fixed costs for the unit will be:

	Yearly	Cents/Lb TCP
Amortization, 10 years	$308,000	0.771
Interest, 12%	237,314	0.593
Maintenance and overhead	462,300	1.156
Taxes and insurance	246,560	0.616
		3.136

Total Manufacturing Costs

Total cost for manufacturing TCP in the facilities described is:

Operating Costs	
Raw materials	60.327
Utilities	0.265
Labor	0.658
Waste disposal	0.429
	61.679
Fixed costs	3.136
	64.815¢/lb TCP

ENVIRONMENTAL MANAGEMENT

In this subsection, the disposal methods, losses, and reclamation process, if any, for each manufacturer of aryl or alkyl aryl phosphate esters will be discussed.

Eastman Kodak Company

The industrial park of Eastman Kodak has industrial waste "sewer" lines leading from each production unit to a centralized treatment plant. Liquid waste streams, resulting from different phases of the production process, are combined into a single waste stream at the production unit. There are two sampling points, one at the production unit site and one at the discharge point into the river.

Liquid waste streams receive primary and secondary (activated sludge) treatment at a centralized unit prior to discharge into an adjacent river. The secondary treatment unit was put into operation in 1970 to remove traces of triphenyl phosphate; prior to that time, only primary treatment (settling and clarification) was utilized before discharge. In the questionnaire (see Appendix A), Eastman Kodak listed the liquid wastes shown below.

Waste	Concentration level	Occurrence
Phenol	0.63%	Process wash water
Triphenyl phosphate	Trace	Process wash water

The hydrogen chloride evolved during the reaction is scrubbed, trapped in water, and recovered as 35% hydrochloric acid. The only impurity in the recovered 35% hydrochloric acid was stated as being 0.002% (maximum) phenol.

Solid waste generated at the industrial park is presently incinerated at 1200° F in a three-chambered incinerator with a water impingement scrubber being utilized to clean the flue gases. In early 1976, a new system for the incineration of solid waste will comprise a rotary kiln with secondary combustion at 1500° to 1800° F. Auxiliary equipment will include a prescrubber quench, high-energy variable throat venturi scrubber, an induced draft fan, a demister, facilities for ash handling and waste material storage, transfer and classification.

Since 1970 the process settling pit sludge, which is the solid residue from the reactor after distillation of the product, has been incinerated. A company spokesman stated that it was unclear as to the method of disposal of this sludge prior to 1970 but that it is probable that the sludge received no treatment and was disposed either in a landfill or the industrial sewer. Impurities in the process settling pit sludge have been stated as being 0.14% phenol and 61% triphenyl phosphate. The

sludge from the biological waste treatment (primary and secondary treatment) is presently, and always has been, smelted for the recovery of silver. This process would, presumably, destroy all organic materials present.

Celanese Corporation

This production facility was purchased by the Stauffer Chemical Company during 1964 and, thus, the environmental management procedures used by this corporation will be the same as those stated for Stauffer during the early stages of the operation of this facility.

FMC Corporation

The environmental management facilities at this production site consist of a centralized covered aerated biological oxidation lagoon and a settling pit prior to discharge into the Kanawha River. As part of a program to clean the Kanawha River, FMC discontinued the production of certain members of its product line in 1965. In 1968, the aerated lagoon was constructed and became operational in the latter part of that year. Prior to 1968, all waste product streams were discharged directly into the Kanawha River without any prior treatment. The segregation of waste materials resulting from the various production units was also initiated as a part of Phase 2 of this program. A methanol recovery system was installed in 1969, but its use was discontinued in approximately 1972 when the production of methyl diphenyl phosphate, as a gasoline additive, was stopped. In Phase 3 of the cleanup plan, an equalization basin was installed and the aeration lagoon was separated into two sections in 1973. The two sections are operated in series with a settling pit between the last lagoon and discharge into the river. Settleable solids from the settling pit are recycled to the lagoon. Nonsetteable solids are discharged into the river. In the production units, indirect condensers have been installed to reduce the volume of water going into the process waste streams. The new Kronitex plant has by-passed the wet refining of the triaryl esters and utilizes a dry processing method which provides for a further decrease of the pollution load through a more efficient process and less waste water in the process waste streams. In the questionnaire, FMC listed 50 to 4,000 ppm phenol and 1 to 40% HC as components in the process waste stream. These stated figures do not represent a variation of that magnitude but rather relate to different sources of process waste streams; e.g., one source may produce a waste stream containing 50 ppm phenol and 1% HCl while another may produce 4,000 ppm phenol and 40% HCl. The potential sources of process waste streams were discussed earlier in this section.

Hydrogen chloride evolved during the reaction is scrubbed, trapped in city water and recovered as 32% hydrochloric acid, which is either consumed in a captive use or sold commercially. The only impurity in the recovered hydrochloric acid was stated as being 1 to 200 ppm phenol.

Solid residues from the reactor, remaining after distillation of the product material, are low volume materials and are currently stockpiled for future disposal. The solid residues were previously disposed in a landfill but this practice ceased when the State of West Virginia changed their landfill permit program.

Mobil Chemical Company

Production at the Edison, New Jersey, facility occurred during the period 1965 to 1970 and was concerned only with the manufacture of relatively small quantities of the phosphate esters. The hydrogen chloride evolved during the reaction process was cleaned and sold. Mr. Brown, the plant manager, also stated that no solid waste was produced by the reaction process.

Monsanto Industrial Chemical Company

Monsanto Industrial Chemicals Company produces several of the phosphate esters selected for investigation. Production takes place at three separate plant sites. In general, the following methods of treatment and their approximate efficiency are employed at one or more of the production facilities: biological oxidation (85 to 90%), absorption and recycle (90 to 95%), and neutralization (100%). Below is a summary of the environmental management techniques employed.

John F. Queeny Plant - St. Louis, Missouri - The production of phosphate esters at this site includes a rather effective phenol recovery system. This recovery system utilizes solvent extraction of the phenol followed by fractional distillation to recover the solvent and phenol. Approximately 90% of the phenol is recovered. The remaining aqueous raffinate contains approximately 100 ppm phenol and small amounts of partial esters. This stream is neutralized and sent to the St. Louis Municipal Sewer District. At present, the Sewer District employs primary treatment before discharging to the Mississippi River. The hydrogen chloride evolved during the reaction is scrubbed and partially used to neutralize in-process streams. The excess acid is sewered. Still residue from the phenol recovery unit is contract incinerated. Final product purification involves filtration with filter aid. The filter aid contaminated with basically final product is landfilled on Company property. The landfill material has passed acute toxicity and leachate test.

Delaware River Plant - Bridgeport, New Jersey - Presently, the aqueous stream from the phosphate ester production department - consisting of HCl from scrubbers, phenol, partial esters, salts, etc. - is combined with other plant waste streams and discharged to the Delaware River. By the third quarter of 1975, the plant will have started up a new activated sludge plant to handle the entire aqueous waste load of the plant; in addition, solvent recovery of phenol is planned. Presently, organic residues from the process are contract incinerated. Also, final product purification filter aid is landfilled on plant property. Plans are to landfill this material at a New Jersey approved landfill when final regulations of solid waste disposal become effective.

W. G. Krummrich Plant - Sauget, Illinois - The process employed at this site produces only one aqueous stream - hydrogen chloride scrubber effluent. No attempt is made to recover this HCl at present and the stream is sewered to the Sauget Treatment Plant which employs primary settling. The Treatment Plant discharges to the Mississippi River. Active plans are to convert the Sauget Treatment Plant to a secondary treatment plant. Solid residues - partial esters, salts, pyrophosphates - are landfilled on Company property after passing acute toxicity and leachate testing.

Sobin Chemicals Incorporated (Montrose Division)

Process waste streams resulting from the manufacturing units are presently collected in storage tanks for further processing. The solid residue remaining after distillation of the product (still bottom) is collected in steel drums and removed from the production site by a licensed scavenger (contract hauler) for disposal in a landfill.

The process waste streams, which have been collected in storage tanks, are processed to recover the hydrogen chloride by passage through a scrubber and absorption in water to produce 20 Bé hydrochloric acid. This hydrochloric acid is either consumed in a captive use or sold commercially. Phenolic and cresylic compounds from the production process are diluted to approximately 0.9 ppm and discharged directly into the Passaic River without further treatment. The Passaic Valley Sewerage Commission monitors the effluent discharge into the river.

Prior to acquisition in mid-1972 by Sobin Chemicals, Inc., the production facility discharged all waste material, including the hydrogen chloride, directly into the Passaic River. Since 1972, the hydrogen chloride recovery system has been added, improvements have been made with regard to the discharge stream into the river and more waste material has been, and will be, accumulated for off-site disposal by a licensed contract hauler.

Stauffer Chemical Company

Currently, this production unit treats the liquid waste streams in a double lagoon system followed by further treatment and recycling into the production process. The liquid wastes, containing 10 to 50 ppm phenols, are initially treated in an aerated lagoon of over 5 acres. Activated sludge settles in this lagoon and requires periodic cleaning. From the first lagoon, the liquid waste is pumped to a second smaller, aerated (1.5 to 2.0 acre) lagoon and then to a 1 acre holding lagoon (2×10^6 gal.). From the holding lagoon, the liquid is gravity-fed to a Calgon carbon treatment system and recycled back into the production process. No liquid discharge of any type is introduced into the Ohio River by this process. A second large lagoon (4.5 acre) is presently in the planning stage. This will allow continuous operation while one lagoon is inoperative for cleaning. Additionally, rotating discs (biological contactors) are currently being tested in the larger lagoon at this production site.

Prior to 1964, Celanese Corporation underwent a series of changes within the production units to improve the recovery of starting materials and hydrogen chloride. However, once the waste stream left the production unit, it was pumped directly into the Ohio River. This procedure remained in effect after the acquisition by Stauffer until 1967 or 1968, when plans for a treatment facility were made. The double lagoon system became operational in late 1969 with the effluent from the second lagoon being discharged into the Ohio River. In mid-January 1975, the recycling process became operational.

As is the case for almost all other production facilities, the hydrogen chloride evolved during the reaction is scrubbed and absorbed in water to form 35% hydrochloric acid, which is sold.

The solid waste, consisting of filter media and the residue from the reactor after product distillation, is disposed in a landfill.

Vulcan Materials Company (Frontier Chemical Division)

This facility formerly was the Kolker Chemical Plant and was an active phosphate ester production facility only in 1964. Since this facility was in operation only the 1 year and was not resold for further use in the production of phosphate esters, no information was obtained concerning their waste management practices.

REFERENCES TO SECTION V

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2. Faith, W. L., D. B. Keyes, and R. L. Clark, Industrial Chemicals, 3rd Ed., pp. 786-787, J. Wiley and Sons (1965).

3. Kirk, R. E., and D. F. Othmer, Eds., Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 15, Interscience Publishers, New York, 1968, pp. 320-321.

SECTION VI

PROCESS TECHNOLOGY

In this section, each of the aryl or alkyl aryl phosphate esters is discussed individually with respect to the various aspects of its manufacturing process and a very brief summary is presented with regard to the usages. Since all of the phosphate esters under consideration are manufactured by basically the same process, no detailed presentation is given with regard to the specific production process for an individual material. A detailed discussion of the general manufacturing process, applicable to all esters, was presented earlier in Section V.

Information relative to each phosphate ester which is presented in this section includes the manufacturing company's corporate address and production site, years of production and production figures, specific preparative reaction, raw materials, type or grade of products, and transportation and handling information.

GENERAL PRODUCTION CAPACITY

The production capacity for each manufacturer of aryl and/or alkyl aryl phosphate esters is given in Table 4. Since all of the actual production facilities are multipurpose plants, a production capacity for a specific ester cannot be provided but will vary considerably dependent upon demand for a specific ester during the year. Under the heading of production years, the year 1964 does not denote that the facility began production in that year but rather that 1964 was the earliest year for the purposes of this report.

The U.S. Tariff Commission Annual Report on Synthetic Organic Chemicals shows Dow Chemical Company as a producer of xenyl diphenyl phosphate during the years 1964 through 1967 and of triphenyl phosphate during 1965. In response to the MRI questionnaire, Dow stated that they did not produce any of the phosphate esters considered for this study. Additional personal

Table 4. PRODUCTION CAPACITY

Manufacturer	Site	Production years	Capacity x 10^6 lb
FMC Corporation	Nitro, West Virginia	1964 to 1974	30
	Nitro, West Virginia	1974 to present	60
Monsanto Industrial Chemicals Company	St. Louis, Missouri Sauget, Illinois	1964 to 1969	40
	Sauget, Illinois Bridgeport, New Jersey St. Louis, Missouri	1969 to present	50
Sobin Chemical Company (Montrose Division)	Newark, New Jersey	1964 to present	12
Stauffer Chemical Company	Gallipolis Ferry, West Virginia	1964 to present	35
Eastman Kodak	Rochester, New York	1964 to present	(5)
Mobil Chemical Company (also: Socony Paint Products and Socony Mobil Oil Company)	Edison, New Jersey	1964 to 1970	(5)
Celanese Corporation	Point Pleasant, West Virginia	1964 sold to Stauffer	(20)
Vulcan Materials Company (Frontier Chemical Division)	Newark, New Jersey	1964	(10)
Dow Chemical Company	Midland, Michigan		
Chevron Chemical Company	Belle Chasse, Louisiana		

Chemical Marketing Reporter, 2 May 1966, 16 August 1969, 17 April 1972, and private industry sources.

() MRI estimate based on information from manufacturers.

contact with Dow resulted in the statement that to their knowledge Dow has never, during the time period of the study, produced either of the two aforementioned materials. Chevron Chemical Company (Additives and Industrial Chemicals Division) is listed in the Tariff Commission Report on Synthetic Organic Chemicals as a producer of dibutyl phenyl phosphate for the years 1969 to present. Response from Chevron stated that they do not manufacture the dibutyl phenyl phosphate. For these reasons, data for the years of production and production capacity have been omitted in Table 4 for Dow Chemical Company and Chevron Chemical Company.

The Celanese Corporation production facility at Gallipolis Ferry, West Virginia, was sold to the Stauffer Chemical Company, who assumed production in October 1964. Thus, the production capacity figures for Stauffer Chemical Company and Celanese Corporation listed in Table 4 for 1964 are, in reality, for the same production facility but with different owners. During subsequent years, the capacity of the facility was increased from approximately 20×10^6 to 30×10^6 lb/year. This does not represent a major expansion of the plant but rather probably a series of de-bottlenecking and other streamlining of the production processes which have gradually occurred over the 10-year span of this report.

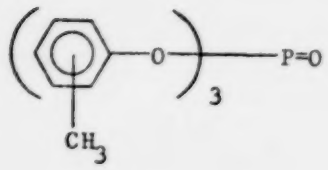
Monsanto Industrial Chemicals Company presently has three plants in operation: Sauget, Illinois; Bridgeport, New Jersey; and St. Louis, Missouri. As shown in Table 4, the Bridgeport facility was first reported in 1969 with a corresponding increase of the combined production capacity from 40×10^6 to 50×10^6 lb/year. This does not represent an actual production capacity for the Bridgeport facility of only 10×10^6 lb/year, but rather a considerable rearrangement in production planning with production responsibilities for selected materials being shifted from the Sauget plant to the new Bridgeport facility and the Sauget plant increasing production of nonphosphate esters with the physical equipment previously used to produce the phosphate esters. These types of switch-offs are feasible since the production facilities are multipurpose plants. Thus, the ultimate total production capacities of these three plants is unknown at the present time but is presumably greater than the listed 50×10^6 lb/year.

Using the figure of 50×10^6 lb/year for Monsanto Industrial Chemicals Company, the present total production capacity for all plants manufacturing phosphate esters is approximately 162×10^6 lb/year.

SPECIFIC PHOSPHATE ESTERS

In this subsection, each phosphate ester will be reviewed with respect to its method of production, manufacturers, raw materials utilized, waste materials produced, trade names, production quantities, and future growth. A brief summary of the areas of use is also presented.

TRICRESYL PHOSPHATE (TCP)



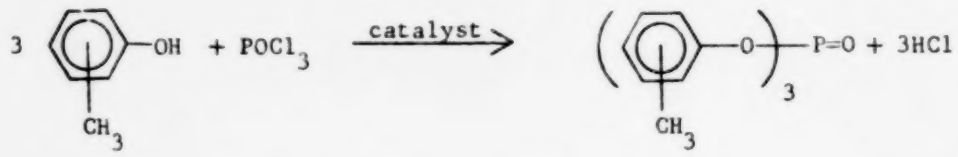
Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Celanese Corporation	New York, New York	Gallipolis Ferry, West Virginia	1964
Vulcan Materials Company (Frontier Chemicals Division)	Wichita, Kansas	Newark, New Jersey	1964
FMC Corporation	New York, New York	Nitro, West Virginia	1964-present
Monsanto Industrial Chemicals Company	St. Louis, Missouri	Sauget, Illinois	1964-present
Sobin Chemical Company	Boston, Massachusetts	Newark, New Jersey	1964-present
Stauffer Chemical Company	Westport, Connecticut	Gallipolis Ferry, West Virginia	1964-present

Production Process

It is very difficult to specify a production process for TCP since many companies manufacture a product which is designated as being TCP but in reality is a complex mixture of several materials. In addition, the cresol (cresylic acid) used as the starting material is normally produced from coal tar refining and is not a pure material. The cresol often contains xylenols, along with many other aromatic phenolic type materials and that there are at least six to eight different "types" of TCP. Most

manufacturers do state that the cresols must contain 1% or less of the ortho isomer but this does not represent a refined material. The process presented below represents an "idealized" situation and in reality is not the actual process which occurs due to the variability in the composition of the cresol starting material.



Required Raw Materials

Basis: 1 ton of tricresyl phosphate		Waste Materials Produced	
Cresylic acid (cresol):	2,001 lb	HCl by-product:	594 lb
Phosphoryl chloride:	946 lb	Sludge:	373 lb
Aluminum chloride:	20 lb		

Energy Consumed

Gas: 1,980 cu ft; steam: 1,049 lb; and electricity: 61.4 kw-hr.

Production Quantities

The production quantities reported in the U.S. Tariff Commission Annual Report on Synthetic Organic Chemicals are inaccurate particularly with regard to the last 4 or 5 years. Almost all manufacturers will add annual production figures for certain materials into the production figures for another material and report the resultant sum as the total production for one of the materials. Tricresyl phosphate is a case in point. Since 1969, the reported annual production figures for TCP also includes annual production figures for isopropylphenyl diphenyl phosphate and trixylenyl phosphate. Some companies regard the isopropylphenyl diphenyl and trixylenyl esters as merely a "type" of tricresyl phosphate and thus do not report them as separate materials.

Year	Celanese	Vulcan	FMC	Monsanto	Sobin	Stauffer	Total quantity x 10^6 lb
1964	(7)	(< 1)	(10)	(11.42)	(1)	(2)	32.4
1965	-	-	(10)	(12.3)	(1)	(11)	34.8
1966	-	-	(12)	(14.3)	(1.5)	(12)	39.8
1967	-	-	(12)	(15)	(1.9)	(14)	42.9
1968	-	-	(13)	(15.3)	(2)	(14)	44.3
1969	-	-	(13)	(15)	(2)	(13.5)	(43.5)
1970	-	-	(11)	(13)	(1.5)	(12.5)	(38.0)
1971	-	-	(10)	(12.8)	(1.5)	(14.5)	(38.8)
1972	-	-	(10)	(8.2)	(1.5)	(17.5)	(37.2)
1973	-	-	(10)	(6.3)	(1.5)	(18)	(35.8)

() = MRI estimate based on information from manufacturers.

Price History[a/]

Year	Price/lb	Total value (million dollars)
1964	$0.27	8.7
1965	0.30	10.4
1966	0.30	11.9
1967	0.31	13.3
1968	0.34	15.1
1969	0.32	13.9
1970	0.33	12.5
1971	0.33	12.8
1972	0.33	12.3
1973	0.36	12.9

a/ U.S. International Trade Commission Annual Reports, 1964 to 1972; 1973 - 1/1/74 issue of Chemical Marketing Reporter.

Trade Names

Stauffer Chemical Company: Lindol (0.1% ortho isomer); Phosflex 179 (plasticizer and lube grade).
Monsanto Industrial Chemicals Company: Generic.
FMC Corporation: Kronitex AA and I.
Sobin Chemicals Company: Generic; electrical and regular grade.

Note: TCP is commonly produced in three grades: plasticizer, lubricant, and electrical. Other grades, such as Lindol (0.1% ortho isomer), are produced for specialty items but would not be considered common grades. Not all manufacturers produce all three common grades, depending upon their markets.

OSHA Standards[1/]

TLV = 0.1 mgm/m^3 of air
8-hr exposure limit for tri-ortho isomer
Test procedure: An impinger in 15 ml of ethylene glycol is used at a test rate of 1 liter/min for 100 min. Analysis is obtained by gas chromatography.

NIOSH Standards[2/]

LDL_o = 1,000 mgm/kg oral - human
TLL_o = 6 mgm/kg oral - human
LDL_o and LD_{50} limits for mixed isomers of TCP may be found in the following reference: NIOSH Toxic Substance List, 1974 edition, p. 608, TC91000 and TD01750.

Physical Properties

Specific gravity at 25° C:	1.160-1.175 at 20° C[3/]	1.157-1.173[4/]
Refractive index at 25° C:	1.553-1.556	
Vapor pressure (mm Hg):	0.50 at 200° C	
Boiling range (° C):	241-255 at 4 mm	420 at 760 mm
Flash point (° C):	225	243
Melting point (° C):	-33	
Viscosity (cp):	78-185 at 20° C	89.0 at 25° C
Density at 25° C; (lb/gal):		9.7

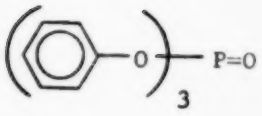
Use Areas

Tricresyl phosphate is presently used extensively in both of the broad categories of functional fluids and fire retardant plasticizers. It also is used as an air filter medium and adhesive for commercial air-conditioning units. During the latter 1950's and early 1960's, it was used extensively as a gasoline additive but later was replaced by cresyl diphenylphosphate for economic reasons.

Future Growth

Tricresyl phosphate, as we have defined the material, apparently is decreasing in usage, particularly in the area of fire retardant plasticizers. Monsanto Industrial Chemicals Company has ceased the commercial sale of this material, although they presumably are still producing some quantities for captive uses such as a lubricant additive and in some hydraulic fluids. One industry source stated that TCP is being used to a very minor extent in polyvinyl chloride and is just holding its own in hydraulic fluids. As other phosphate esters such as isopropylphenyl diphenyl and Monsanto's proprietary mixture increase their share of the hydraulic fluid market, TCP will find decreasing utility in this area. Due to TCP's high cost and reliance on the availability of cresylic acid, substitutes are being sought for TCP in the lubricant additives area. This has been one area where TCP was the dominant phosphate ester but apparently will begin to suffer decreasing utility in this field. By 1984 it is conceivable that, with new products being developed, tricresyl phosphate will be produced only in very small quantities for specialty items. Assuming that TCP will still be used to a certain extent as a fire resistant hydraulic fluid and lubricant additive, an annual production of 12 to 16 million pounds in 1984 is probably reasonable.

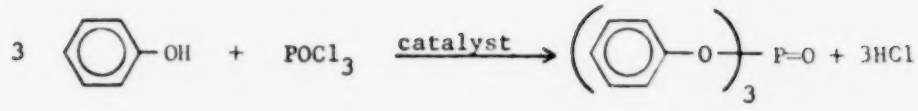
TRIPHENYL PHOSPHATE



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Celanese Corporation	New York, New York	Gallipolis Ferry, West Virginia	1964
Eastman Kodak	Rochester, New York	Rochester, New York	1964-present
Monsanto Industrial Chemicals Company	St. Louis, Missouri	Sauget, Illinois	1964-present
Sobin Chemicals Company (Montrose Division)	Boston, Massachusetts	Newark, New Jersey	1967
Stauffer Chemical Company	Westport, Connecticut	Gallipolis Ferry, West Virginia	1964-1973

Production Process



Required Raw Materials (88% yield)

Basis: 1 ton of triphenyl phosphate		Waste Materials Produced	
Phenol:	1,966 lb	HCl by-product:	671 lb
Phosphoryl chloride:	1,068 lb	Sludge:	383 lb
Zinc chloride:	20 lb		

Energy Consumed

Gas: 1,980 cu ft; steam: 1,049 lb; and electricity: 61.4 kw-hr.

Production Quantities

Year	Celanese	Eastman Kodak Company	Monsanto	Stauffer	Sobin	Total quantity[6] x 10^6 lb
1964	(2.5)	(2.7)	(3.3)	(0.5)	-	9.0
1965	-	(2.7)	(3.1)	(3.1)	-	(8.9)
1966	-	(2.7)	(3.1)	(3)	-	8.8
1967	-	(2.6)	(3)	(3)	(0.1)	8.7
1968	-	(2.4)	(2.7)	(2.8)	-	7.9
1969	-	(2.8)	(3.2)	(3.2)	-	9.2
1970	-	(3.2)	(3.3)	(4.1)	-	10.6
1971	-	(3.2)	(3.3)	(4)	-	(10.5)
1972	-	(3.3)	(4.7)	(3)	-	(11)
1973	-	(3.5)	(6.5)	(2)	-	(12)

( ) = MRI estimate based on industry estimates.

Price History

Year	Price/lb	Total value (million dollars)
1964	$0.36[a/]	3.2
1965	0.415	3.7
1966	0.415	3.7
1967	0.415	3.6
1968	0.415	3.3
1969	0.415	3.8
1970	0.415	4.4
1971	0.415	4.4
1972	0.37	4.1
1973	0.37	4.4

a/ U.S. International Trade Commission data; all other prices are from December issues of Chemical Marketing Reporter.

Trade Names

Stauffer Chemical Company: Phosflex TPP.
Monsanto Industrial Chemicals Company: Generic.
Eastman Kodak Company: Generic.
Sobin Chemical Company: Generic.

OSHA Standards[1/]

TLV = 3 mgm/m^3 of air
8-hr exposure limit; sampled as a dust rather than vapor.

Test Procedure

An impinger in 15 ml of ethylene glycol is used at a test rate of 1 liter/min for 100 min. Analysis obtained by gas chromatography.

NIOSH Standards[5/]

TCL_o: 3.0 mgm/m^3 (human inhalation)

Physical Properties

Specific gravity at 25° C: 1.185-1.202[3/]
Refractive index at 25° C: 1.552-1.563 1.550 at 60° C

Flash point (°C):	225	
Vapor pressure (mm Hg):	190 at 200° C	
Boiling range (°C):	220 at 5 m	370 at 760 mm[4/]
Melting point (°C):	49.2	48.5[4/]
Viscosity (cp):	9.9 at 55° C	7.8 at 55° C[4/]
Density at 25° C (lb/gal):		10.5[4/]

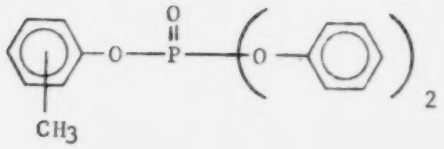
Use Areas

At the present time triphenyl phosphate is used exclusively as a plasticizer primarily with cellulosics, such as cellulose acetate and cellulose nitrate. It also finds use in the newer rigid thermosetting materials, such as polyphenylene oxide, and in synthetic rubbers. In the mid-1960's (1964 to 1966), Shell Oil Company used it as an additive to their motor oil.

Future Growth

The production of triphenyl phosphate from 1949 to 1973 increased at an average growth rate of 4.4%/year. Industry sources indicate that, barring any unforeseen circumstances, the growth should continue as in the past since TPP is regarded as a type of speciality plasticizer, i.e., does not have a universal-type application area. This limitation in use area is due to the fact that TPP is a solid and would present problems in the formulation and processing of several resins. Projected production figures, based upon a 4 to 5% yearly growth rate after 1975, would indicate an annual production of 15.5 to 17 million pounds by 1984.

CRESYL DIPHENYL PHOSPHATE (CDP)

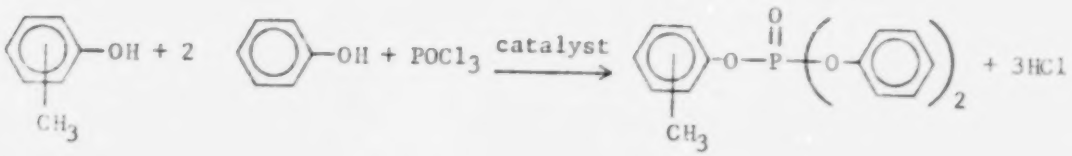


Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Celanese Corporation	New York, New York	Gallipolis Ferry, West Virginia	1964
FMC Corporation	New York, New York	Nitro, West Virginia	1964-present
Monsanto Industrial Chemical Company	St. Louis, Missouri	Sauget, Illinois	1964-present
Sobin Chemical Company	Boston, Massachusetts	Newark, New Jersey	1964-present
Stauffer Chemical Company	Westport, Connecticut	Gallipolis Ferry, West Virginia	1964-present
Mobil Chemical Company*	Richmond, Virginia	Edison, New Jersey	1964-1970

* Same as Socony Paint Products (1964) and Socony Mobil Oil Company (1964-1970).

Production Process



Required Raw Materials (88% yield)

Basis: 1 ton of cresyl diphenyl phosphate		Waste Materials Produced	
Cresylic acid:	718 lb	HCl by-product:	677 lb
Phenol:	1,250 lb	Sludge:	329 lb
Phosphoryl chloride:	1,018 lb		
Aluminum chloride:	20 lb		

Energy Consumed

Gas: 1,980 cu ft; steam: 1,049 lb; and electricity: 61.4 kw-hr.

Production Quantities

Year	Celanese	Mobil	FMC	Monsanto	Sobin	Stauffer	Total quantity x 10^6 lb[7]
1964	(2.5)	(4)	(3)	(4.5)	(1.6)	(0.5)	16.1
1965	-	(5)	(3.5)	(5.7)	(2.0)	(3.5)	19.7
1966	-	(5)	(3.5)	(6)	(2.0)	(3.5)	20.0
1967	-	(4)	(3)	(5.9)	(1.8)	(3.5)	18.2
1968	-	(3)	(4)	(6.8)	(2.0)	(4)	19.8
1969	-	(2)	(2)	(4.1)	(1.0)	(2)	11.1
1970	-	(2)	(2)	(4.4)	(1.3)	(3)	12.7
1971	-	-	(4)	(8.4)	(2.0)	(6)	20.4
1972	-	-	(2)	(7.1)	(1.5)	(4)	14.6
1973	-	-	(2)	(8.7)	(1.5)	(2)	14.2

( ) = MRI estimate based on production capacities.

Mobil Chemical stated that all of their CDP was used only in a captive process as a gasoline additive and that production ranged from approximately 5 x 10^6 lb during the mid-1960's to approximately 2 x 10^6 lb at the end of the use of phosphate esters as gasoline additives. Other manufacturing sources feel that Mobil's captive use could not have exceeded 3 million pounds in any year and that any quantities over this figure were sold to other companies as a gasoline additive (e.g., Shell Oil Company).

Price History[a/]

Year	Price/lb	Total value (million dollars)
1964	$0.25	4.0
1965	0.26	5.1
1966	0.26	5.2
1967	0.28	5.1
1968	0.28	5.5
1969	0.27	3.0
1970	0.27	3.4
1971	0.25	5.1
1972	0.27	3.9
1973	0.27	3.8

a/ U.S. International Trade Commission data.

Trade Names

Stauffer Chemical Company: Phosflex 122.
Monsanto Industrial Chemicals Company: Santicizer 140.
Sobin Chemicals Company: Generic.
FMC Corporation: Kronitex MX, Kronitex K-3*

Physical Properties

Specific gravity at 25°C:	1.204-1.208[3/]	
Refractive index at 25°C:	1.560	
Flash point (°C):	233-237	
Vapor pressure (mm Hg):	0.08 at 200°C	
Boiling range (°C):	253 at 10 mm	390 at 760 mm[4/]
Melting point (°C):	-38	
Viscosity (cp):	33.0 at 25°C	
Density at 25°C (lb/gal):	10.0[4/]	

* Kronitex K-3 is a mixed phosphate ester containing cresylic and phenolic groups in varying ratios probably dependent upon the desired viscosity for the final product. Most likely a mixture of cresyl diphenyl and dicresyl phenyl phosphate in variable ratios.

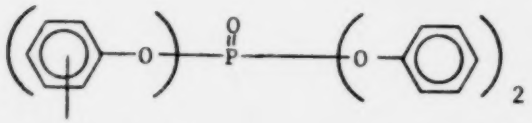
Use Areas

Cresyl diphenyl phosphate presently is used extensively in both the broad categories of functional fluids and fire retardant plasticizers. During the 1960's and very early 1970's, it was used as a preignition control additive in gasoline.

Future Growth

While the growth of fire retardant plasticizers and functional fluids will probably increase over the next 10 years, but not at the rate observed for the past 3 to 4 years. This growth probably will come at the expense of CDP. Cresyl diphenyl phosphate is considered one of the "old-line" plasticizers and hydraulic fluid components and is being replaced by newer materials in both fields. The apparent decision by Monsanto Industrial Chemicals Company to cease production of CDP during (or at the end of) 1975 is probably indicative of the relative future growth for this material. While usage of this material will not cease totally, it is difficult to predict a positive growth unless new areas of usage are created. For this reason, a gradual decrease of 2 to 4%/year has been predicted. However, if other manufacturers follow the lead of Monsanto, the decrease could be even more rapid than predicted. The annual production figures for 1975 and 1976 could be very indicative of the future of cresyl diphenyl phosphate. The projected annual production in 1984 is approximately 8.4 to 10.6 million pounds.

ISOPROPYLPHENYL DIPHENYL PHOSPHATE*



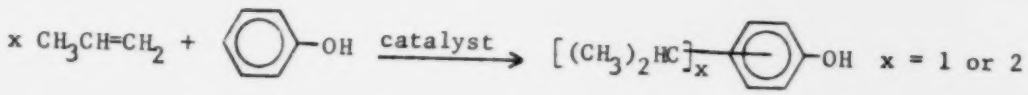
$[CH(CH_3)_2]_x$ X = 1 or 2

* Throughout this report, this name will be utilized in all discussions and tables. Although this name is the specific compound that is closest to the actual product, the different grades represent different ratios of isopropylphenols to phenol and the term "mixed isopropylphenyl phenyl phosphate" is a more accurate representation.

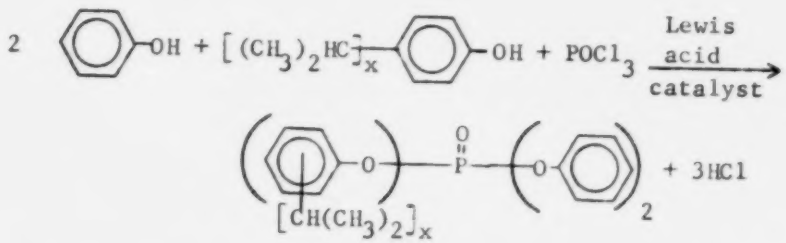
Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
FMC Corporation	New York, New York	Nitro, West Virginia	1969-present
Stauffer Chemical Company	Westport, Connecticut	Gallipolis Ferry, West Virginia	1971-present

Production Process



Freidel-Craft type alkylation. The mono-, or disubstituted, or mixture of mono- and disubstituted phenols are produced depending upon the desired viscosity of the final product.



Required Raw Materials (88% yield)

Basis: 1 ton of isopropylphenyl diphenyl phosphate.

	Mono-subst.	Di-subst.
Isopropylphenol:	837 lb	990 lb
Phenol:	1,158 lb	1,039 lb
Phosphoryl chloride:	943 lb	847 lb
Aluminum chloride:	20 lb	20 lb

Waste Materials Produced

	Mono-	Di-
HCl by-product:	592 lb	532 lb
Sludge:	366 lb	364 lb

Energy Consumed

Gas: 1,980 cu ft; steam: 1,049 lb; and electricity: 61.4 kw-hr.

Production Quantities

Year	FMC	Stauffer	Total quantity x 10^6 lb	Price/lb ($)	Net value (million dollars)
1969	(3)	-	(3)	0.29	0.9
1970	(5)	-	(5)	0.29	1.5
1971	(7)	(1)	(8)	0.29	2.3
1972	(11)	(1)	(12)	0.29	3.5
1973	(16)	(2)	(18)	0.29	5.2

( ) = MRI estimate based on industry sources.

Trade Names

FMC: Kronitex 100

For reporting purposes to the U.S. Tariff Commission, FMC has always added the yearly production figures for the isopropylphenyl diphenyl phosphate into the figures they reported for tricresyl phosphate. Thus, the figures quoted in the Tariff Commission Report on Synthetic Organic Chemicals for TCP are not true values for TCP alone but also contain figures for other phosphate esters, notably the one discussed here and trixylenyl phosphate.

Physical Properties

Specific gravity at 25° C:	1.150-1.165[3/]
Refractive index at 25° C:	1.552[3/]
Flash point (° C):	230[3/]
Vapor pressure (mm Hg):	-
Boiling range (° C):	220-270[3/]
Melting point (° C):	-
Viscosity (cp):	-
Density at 25° C (lb/gal):	(9.5-9.7)

( ) = MRI estimate.

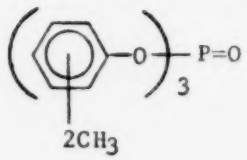
Use Areas

Minor quantities of isopropylphenyl diphenyl phosphate were imported by FMC Corporation from Ciba-Geigy in England prior to its production in the United States. During the period of importation and the early years of its production in the United States, it was used primarily in the formulation of hydraulic fluids. However, in the last 3 to 4 years, its use as a fire retardant plasticizer has increased steadily. In 1973 approximately 50% of the production of isopropylphenyl diphenyl phosphate was for use as a plasticizer. Small quantities may also be used in the field of lubricant additives

Future Growth

The growth of isopropylphenyl diphenyl phosphate is expected to increase at a steady rate, although not at the same rate as for the last 5 years. If the synthetic fluids area of fire resistant hydraulic fluids continues to grow at the predicted rate, then the production of isopropylphenyl diphenyl phosphate will increase at the same or faster rate. With the addition of Stauffer Chemical Company as a producer, this material could make further inroads into that portion of the synthetic fire resistant hydraulic fluids market now held by other triaryl phosphates, i.e., tricresyl phosphate, cresyl diphenyl phosphate, and trixylenyl phosphate. In the area of fire retardant plasticizers, isopropylphenyl diphenyl phosphate should continue to replace materials such as TCP and CDP. Overall, isopropylphenyl diphenyl phosphate could be expected to grow at an average annual rate of approximately 11 to 13%/year after 1975. If tricresyl phosphate and cresyl diphenyl phosphate show sharp decreases in production, this rate could increase more rapidly than predicted. The projected figures for the average annual production, based on 11 to 13%/ year, would lead to an annual production of 39 to 49 million pounds in 1984.

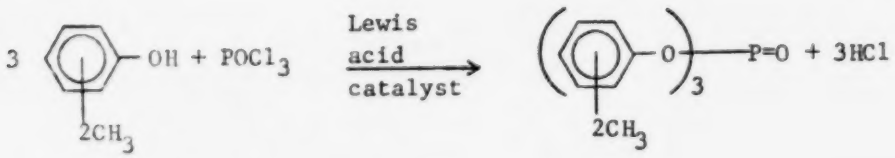
TRIXYLENYL PHOSPHATE



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
FMC Corporation	New York, New York	Nitro, West Virginia	1970-present

Production Process



FMC considers this material to be a high molecular weight, low specific gravity grade of TCP. No 2,6-isomers are present in the product. The most reactive isomers are the 3,5 (m,m) and 3,4 (m,p) and the final product is a mixture of these two isomers.

Required Raw Materials (88% yield)

Basis: 1 ton of trixylenyl phosphate		Waste Material Produced	
Xylenol:	2,028 lb	HCl by-product:	533 lb
Phosphoryl chloride:	849 lb	Sludge:	364 lb
Aluminum chloride:	20 lb		

Energy Consumed

Gas: 1,980 cu ft; steam: 1,049 lb; and electricity: 61.4 kw-hr.

Production Quantities

Year	Total quantity x 10^6 lb*	Price/lb ($)	Net value (million dollars)
1970	(3)**	0.32	1.0
1971	(2)	0.34	0.7
1972	(1)	0.34	0.3
1973	(2)	0.36	0.7

Trade Names

FMC: Kronitex TXP.

Physical Properties

Specific gravity at 25° C:	1.130-1.145[3]
Refractive index at 25° C:	1.551-1.555[3]
Flash point (° C):	235[3]
Vapor pressure (mm Hg):	-
Boiling range (° C):	270 at 3 mm[3]
Melting point (° C):	-35 (pour point)[3]
Viscosity (cp):	190 at 20° C[3]
Density at 25° C (lb/gal):	(9.4-9.6)

Use Areas

Trixylenyl phosphate is used almost exclusively in the formulation of fire retardant hydraulic fluids and lubricant additives.

Future Growth

Trixylenyl phosphate is considered one of the "old-line" fire resistant hydraulic fluids, along with tricresyl phosphate and cresyl diphenyl phosphate. In view of the apparent static growth potential of these older materials in the fluids area, it would be difficult to predict any significant increase in production quantities for trixylenyl phosphate. If areas of application as a fire retardant plasticizer could be found, perhaps the production could increase. However, this material has been

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( ) = MRI estimate.

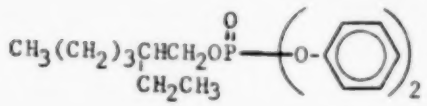
* FMC Corporation could have imported some of this quantity; most likely from Ciba-Geogy in England.

** In Section IV, Table 1, the quantities for the years 1970 to 1973 are included with TCP.

on the market for at least 4 years and any increased usage as a plasticizer would be at the expense of established materials and/or any new product. It does not appear likely that this new growth will materialize. It is estimated that the production quantities will remain relatively constant at approximately 2 million pounds per year for the next 10 years.

2-ETHYLHEXYL DIPHENYL PHOSPHATE

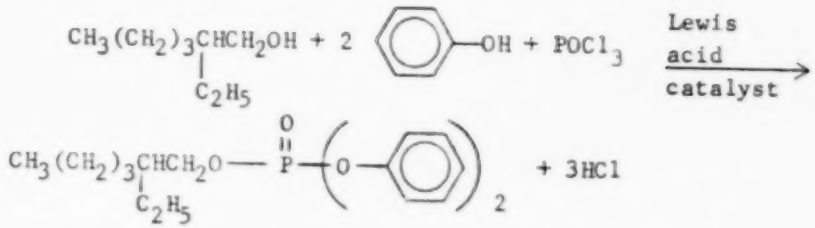
(Octyl Diphenyl Phosphate)



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Monsanto Industrial Chemicals Company	St. Louis, Missouri	Bridgeport, New Jersey	1968-present
		St. Louis, Illinois	1964-present

Production Process



Two-step process. Diaryl phosphoryl chloride intermediate not isolated.

Required Raw Material (88% yield)

Basis: 1 ton of octyl diphenyl phosphate

2-Ethylhexanol:	816 lb
Phenol:	1,181 lb
Phosphoryl chloride:	962 lb
Aluminum chloride:	20 lb

Waste Materials Produced	
HCl by-product:	604 lb
Sludge:	375 lb

Energy Consumed

Gas: 2,772 cu ft; steam: 1,049 lb; and electricity: 71.3 kw-hr.

Production Quantities

Year	Total quantity x 10^6 lb	Estimated price/lb ($)	Estimated net value (x 10^6 dollars)
1964	(9)	0.35	3.2
1965	(9)	0.35	3.2
1966	(8)	0.35	2.8
1967	(8)	0.35	2.8
1968	(5)	0.35	1.8
1969	(4)	0.35	1.4
1970	(4)	0.35	1.4
1971	(3)	0.35	1.1
1972	(3)	0.35	1.1
1973	(5)	0.36	1.8

( ) = MRI and industry contact estimates.

Trade Names

Monsanto: Santicizer 141.

NIOSH Standard[6]

LDL_o = 272 mg/kg IVN-rbt

Physical Properties

Specific gravity at 25° C:	1.08-1.09[3]
Refractive index at 25° C:	1.506-1.512[3]
Flash point (° C):	200[3]
Vapor pressure (mm Hg):	1.3 at 200° C[4]
Boiling point (° C):	375[4]
Melting point (° C):	-6[3]
Viscosity (cp):	21-23[4]; 16.4 at 25° C[4]
Density at 25° C (lb/gal.):	9.1[4]

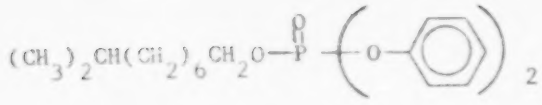
Use Areas

2-Ethylhexyl diphenyl phosphate is used principally as a plasticizer for synthetic rubbers and plastics. It is regulated under the provisions of the U.S. Food and Drug Administration for use in adhesive and in certain coatings for food products. This product is also utilized in the formulation of fire resistant functional fluids (hydraulic fluids).

Future Growth

Future production quantities of this material should proceed at a pace consistent with the anticipated growth for each of the areas of plasticizers and hydraulic fluids. This would project an average future growth of approximately 8 to 10%/year after 1975, and show an annual production of 8.5 to 10 million pounds in 1984.

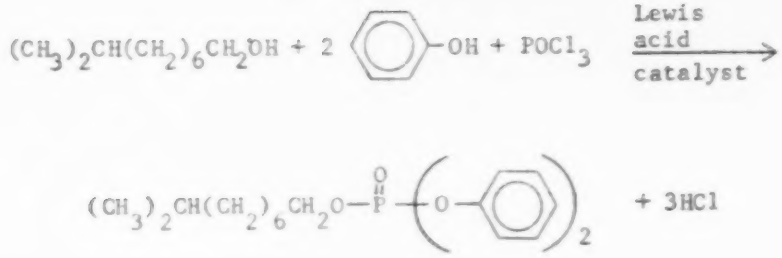
ISODECYL DIPHENYL PHOSPHATE



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Monsanto Industrial Chemicals Company	St. Louis, Missouri	Bridgeport, New Jersey	1968-present

Production Process



Two-step process. Diaryl phosphoryl chloride intermediate not isolated.

Required Raw Material (88% yield)

Basis: 1 ton of isodecyl diphenyl phosphate		Waste Materials Produced	
Isodecyl alcohol:	921 lb	HCl by-product:	560 lb
Phenol:	1,095 lb	Sludge:	368 lb
Phosphoryl chloride:	892 lb		
Aluminum chloride:	20 lb		

Energy Consumed

Gas: 2,772 cu ft; steam: 1,049 lb; and electricity: 71.3 kw-hr.

Production Quantities

Year	Total quantity x 10^6 lb	Estimated price/lb ($)	Estimated net value (x 10^6 dollars)
1968	(1.0)	0.275	0.3
1969	(2.0)	0.275	0.6
1970	(4.0)	0.275	1.1
1971	(4.5)	0.275	1.2
1972	(5.0)	0.275	1.4
1973	(7.0)	0.285	2.0

( ) = MRI and industry contact estimates.

Trade Names

Monsanto: Santicizer 148.

Physical Properties

Specific gravity at 25° C:	1.07[3]	
Refractive index at 25° C:	1.506[3]	
Flash point (° C):	241	
Vapor pressure (mm Hg):	0.5 at 200° C[3]	10.0 at 200° C[4]
Boiling range (° C):	245 at 10 mm[3]	
Melting point (° C):	-	
Viscosity (cp):	22.5 at 25° C[3]	
Density at 25° C (lb/gal):	8.9[4]	

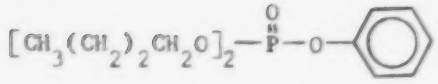
Use Areas

Isodecyl diphenyl phosphate is used principally as a fire retardant plasticizer for plastics and synthetic rubbers.

Future Growth

Since isodecyl diphenyl phosphate finds rather general usage as a fire retardant plasticizer, particularly where low temperature flexibility is a factor, it would be expected that the future production of this material would approximate that for fire retardant plasticizers in general. Thus, an average annual growth rate of approximately 7 to 9%/year could be anticipated after 1975. At this average annual growth rate, the production quantity in 1984 would be approximately 11 to 13 million pounds.

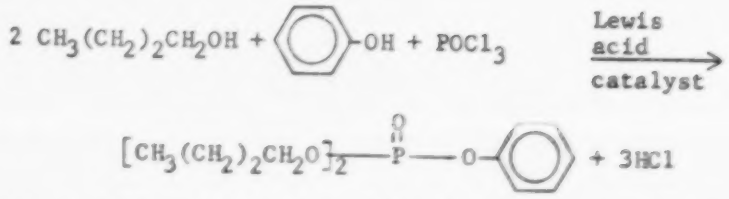
DIBUTYL PHENYL PHOSPHATE



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Monsanto Industrial Chemicals Company	St. Louis, Missouri	St. Louis, Missouri	1964-present

Production Process



Two-step process. Aryl phosphoryl dichloride intermediate not isolated.

Required Raw Material (88% yield)

Basis: 1 ton of dibutyl phenyl phosphate	
1-Butanol:	1,176 lb
Phenol:	747 lb
Phosphoryl chloride:	1,217 lb
Aluminum chloride:	20 lb

Waste Materials Produced	
HCl by-product:	764 lb
Sludge:	396 lb

Energy Consumed

Gas: 2,772 cu ft; steam: 1,049 lb; and electricity: 71.3 kw-hr.

Production Quantities

Year	Total quantity x 10^6 lb[a/]	Estimated price/lb[b/] ($)	Estimated net value (x 10^6 dollars)
1964	(1.6)	0.36	0.6
1965	(1.8)	0.36	0.6
1966	(2.0)	0.36	0.7
1967	(2.4)	0.36	0.9
1968	(2.8)	0.36	1.0
1969	(2.3)	0.36	0.8
1970	(2.5)	0.36	0.9
1971	(2.7)	0.36	1.0
1972	(2.9)	0.36	1.0
1973	(3.1)	0.37	1.1

a/ As will be discussed in Section VII-A (aircraft hydraulic fluids), it is felt that these values are low by 50 to 60%.

b/ Price estimated on the basis of annual raw material costs and price markup of other alkyl aryl compounds.

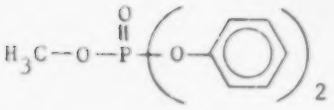
Use Areas

Dibutyl phenyl phosphate is used almost exclusively in commercial aircraft hydraulic fluid formulations. It is possible that very small quantities may be used in industrial hydraulic fluids.

Future Growth

This phosphate ester is directly dependent upon the commercial airline industry and its future growth will be linked to that industry. The current manufacturer of dibutyl phenyl phosphate anticipates a future growth rate of 5 to 7%/year. It is doubtful that this growth rate was attained in 1974 or will be in 1975, however, after 1975 this growth rate could be assumed. The annual production in 1984 would be in the range of 5 to 6 million pounds per year based upon the production figures in this subsection and an average annual growth rate of 5 to 7%. If the stated production figures are low by 50%, then the projected annual production in 1984 would be 7 to 8.5 million pounds. FMC Corporation has recently begun production of dibutyl phenyl phosphate and their entry into the market could increase the production quantities of this material higher than the predicted figures.

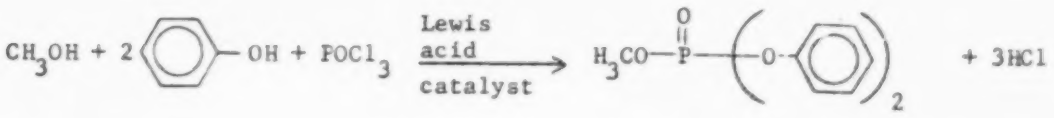
METHYL DIPHENYL PHOSPHATE



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Monsanto Industrial Chemicals Company	St. Louis, Missouri	St. Louis, Missouri	1964-1971
FMC Corporation	New York, New York	Nitro, West Virginia	1964-1971

Production Process



Two-step process. Diaryl phosphoryl chloride intermediate not isolated.

Required Raw Materials (88% yield)

Basis: 1 ton of methyl diphenyl phosphate	
Methanol:	275 lb
Phenol:	1,619 lb
Phosphoryl chloride:	1,318 lb
Aluminum chloride:	20 lb

Waste Materials Produced	
HCl by-product:	828 lb
Sludge:	404 lb

Energy Consumed

Gas: 2,772 cu ft; steam: 1,049 lb; and electricity: 71.3 kw-hr.

Production Quantities

Year	Monsanto	FMC	Total quantity x 10^6 lb
1964	(2.4)	(2.4)	(4.8)
1965	(2.9)	(2.9)	5.8
1966	(2.9)	(2.9)	(5.8)
1967	(2.9)	(3.0)	(5.9)
1968	(2.9)	(3.0)	(5.9)
1969	(3)	(3)	6.0
1970	(1)	(1)	(2.0)
1971	(0.5)	(0.5)	(1.0)

( ) = MRI estimates; other data supplied by Mr. Paul Levesque, FMC Corporation, New York, New York.

Price History

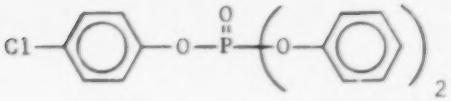
Year	Estimated price/lb[a/]	Estimated total value (million dollars)
1964	$0.31	1.5
1965	0.31	1.8
1966	0.31	1.8
1967	0.31	1.8
1968	0.31	1.8
1969	0.31	1.9
1970	0.30	0.6
1971	0.30	0.3

a/ Price estimated on the basis of annual raw material costs and price markup of other alkyl aryl compounds.

Use Area

During the years 1964 to 1971, methyl diphenyl phosphate was used almost exclusively as a preignition control gasoline additive. In a recent book concerning flame retardancy of polymers,[9/] this material was listed as a plasticizer for vinyl films; however, this use probably accounted for only a very minor part of its total usage during that time interval.

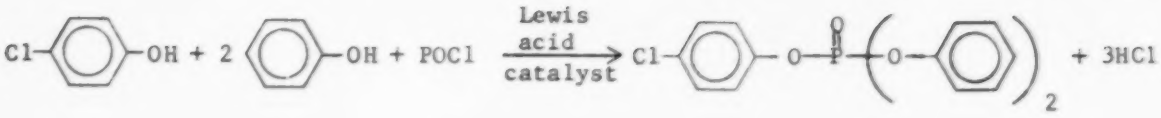
p-CHLOROPHENYL DIPHENYL PHOSPHATE



Manufacturers

Manufacturer	Corporation office site	Production site	Years produced
Monsanto Industrial Chemicals Company	St. Louis, Missouri	St. Louis, Missouri	1968-1969

Production Process



Production Quantities

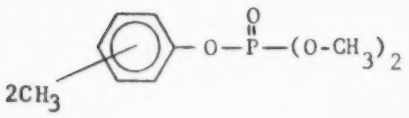
Year	Total quantity x 10^6 lb
1968	($\ll$ 0.1)
1969	($\ll$ 0.1)

( ) = MRI estimate based on manufacturer's information.

Use Area

The p-chlorophenyl diphenyl ester was produced with the intention of introducing it into the fire retardant plasticizer field. However, in actual usage, the material showed rather poor heat stability properties and was never a competitive plasticizer. Monsanto ceased production after 2 years and no further production or usage of this material is known.

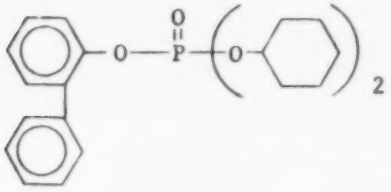
DIMETHYL XYLYL PHOSPHATE



Two patents have been issued for the use of this material: one in 1958 for use as an anti-knock additive fluid[10/] and one in 1970 for use as an anti-wear jet fuel additive.[11/]

Industrial sources[12/] indicate that they are unaware of any company who has produced or is currently producing this material on a commercial basis. It is possible that small quantities of this ester were produced in the latter 1950's or very early 1960's as a gasoline additive. If this was the case, the ester never received any widespread usage and very possibly was produced in very small quantities for the company's captive use.

MONO-O-XENYL DIPHENYL PHOSPHATE



The U.S. Tariff Commission Reports[13/] show that this material was produced by Dow Chemical Company during the years 1964 to 1967. Dow Chemical Company has stated, in both written and oral communication, that they do not and never have produced any of the phosphate esters of interest to this study including specifically the mono-o-xenyl diphenyl phosphate ester.

The National Institute for Occupational Health and Safety[14/] lists a LDL_o value of 50 mg/kg (mice) for this ester.

MIXED ALKYL ARYL PHOSPHATES

Monsanto Industrial Chemicals Company manufactures an alkyl aryl phosphate for use as a component in hydraulic fluids and as a plasticizer. It is a complex mixture resulting from the use of nonyl alcohol, isodecyl alcohol, phenol, cumenol, and perhaps some additional higher molecular weight alcohols in the C_8-C_{10} range. The exact composition of this fluid is variable dependent upon the viscosity requirements of the particular customer for the finished material. For use as a plasticizer, Monsanto distributes this material under the trade name of Santicizer 145.

TRANSPORTATION AND HANDLING

The Code of Federal Regulations, Title 49, Transportation (1 October 1973) does not list any of the phosphate esters contained in this report as being hazardous materials and no special labeling or handling of the shipping containers is required. A revised Section 311 (b)(2)(B) of the Federal Water Pollution Control Act Amendments of 1972 (Federal Register, 22 August 1974) also does not list any of these phosphate esters as being hazardous substances.

Within the production facility, the finished product is pumped to storage tanks for packaging or bulk shipment. All transfers of the esters from the storage tanks to packaging are conducted through pipelines and no appreciable quantitites of the esters are handled or transported in open containers. The packaging area is the only place where contact with the ester would occur and that would happen basically through broken or leaking containers.

When packaged for shipment, the phosphate esters are normally packaged and shipped in either 55 gal. unlined steel drums, railway tankcars, or truck tankwagons. One manufacturer estimated that 60% of their shipments were in bulk quantities (tankcar or tankwagon) and 40% were in steel drums. Triphenyl phosphate, a solid, is normally shipped in either 250 lb fiber drums or 1,200 lb reinforced cardboard containers. Both of these containers are lined on the interior with plastic sheeting. Experimental quantities are available in smaller containers but the quantity shipped is negligible compared to the other methods.

REFERENCES TO SECTION VI

1. Private communication with Mr. Charles Adkins, OSHA Regional Office, Kansas City, Missouri.

2. "NIOSH Toxic Substances List," p. 608, 1974 ed., TD 03500.

3. Modern Plastics Encyclopedia, McGraw-Hill, Inc., New York, p. 781 (1974-1975).

4. Monsanto Industrial Chemicals Company, "Fire Retardant Plasticizers and Resin Modifiers," Bulletin IC/PL-358, July 1974.

5. "NIOSH Toxic Substances List," p. 746, 1974 ed., 18972; see also p. 608, TC 84000.

6. U.S. International Trade Commission Annual Report, "Synthetic Organic Chemicals," (1964, 1966-1970).

7. U.S. International Trade Commission Annual Report, "Synthetic Organic Chemicals," (1964-1973).

8. "NIOSH Toxic Substances List," p. 607, 1974 ed., TC 61250.

9. Kuryla and Papa, Flame Retardancy of Polymeric Materials, Marcel Dekkar, New York (1973).

10. Ethyl Corporation, Brit. 872820, 9 December 1958; CA, 56, 6250i (1962).

11. Vermillion, H. E., and G. W. Eckert (Texaco, Inc.), U.S. 3,510,281, 5 May 1970; CA, 73, 17150d (1970).

12. Industrial Source, private communication.

13. U.S. International Trade Commission, "Synthetic Organic Chemicals" (1964-1967).

14. "NIOSH Toxic Substances List," p. 605, 1973 ed., TB 66500.

SECTION VII

AREAS OF UTILIZATION

In this section, each of the primary areas of utilization for the general group of aryl and alkyl aryl phosphate esters under consideration will be discussed. The main areas of hydraulic fluids and lubricant additives, fire retardant plasticizers, and gasoline additives (area ceased in 1971) will be discussed as separate sections and minor use areas such as exports, wood preservatives, air filter media, and others will be treated individually but under the general subsection of Miscellaneous Uses.

HYDRAULIC FLUIDS AND LUBRICANT ADDITIVES

The discussion of hydraulic fluids and lubricant additives will be separated into three sections; (a) general hydraulic fluids; (b) aircraft hydraulic fluids; and (c) lubricant additives. Aircraft hydraulic fluids will be treated separately because only one of the phosphate esters under study is utilized in aircraft hydraulic systems whereas most of the phosphate esters find usage in the general hydraulic fluid field.

Industrial Hydraulic Fluids

The general field of hydraulic fluids can be divided into the two primary sections of petroleum-based fluids and fire resistant fluids. Shortly after their introduction in the late 1940's, users became disenchanted with the poor performance of the phosphate esters compared to petroleum fluids. Some portion of this disenchantment may have been due to the misapplication of the fluids or to faulty hydraulic system design. Regardless of the specific reasons, this initial experience had an inhibiting effect on the acceptance, and thus the sales growth, of fire resistant fluids. By 1966, fire resistant fluids had claimed only about 6% of the total market.[1/] A survey published in mid-1965 showed fire resistant fluids with approximately 6% of the total market for hydraulic fluids.[2/] From mid-1965, however, a resurgent interest in fire retardant fluids occurred as evidenced by a new edition of this survey in 1970,[3/] which showed fire resistant fluids to have approximately 22% of the total hydraulic fluids market. This latter figure, at least combined with the data for phosphate esters, is probably too high and will be discussed in more detail later in this section.

The classification of fire resistant hydraulic fluids is comprised basically of four "types" of materials: (a) water-glycol systems; (b) water-hydrocarbon oil emulsions; (c) phosphate esters; and (d) phosphate ester-hydrocarbon oil blends.[4,5] The groupings of phosphate esters and the phosphate ester-hydrocarbon blends are often termed "synthetics" or "synthetic fluids" and "oil-synthetic blends."

The results published in the two surveys,[2,3] and tabulated below, shows the percentage distribution of the usage of fire resistant hydraulic fluids in 1964 and 1970. The number of plants responding to this survey was relatively small, both with respect to the overall field of hydraulic fluids and to the fire resistant fluids. However, the percentage values should be useful in the prediction of trends within the category of fire resistant fluids.

Type of fire resistant fluid	1964	1970
Emulsion:		
Total	46.8%	47.1%
Oil-in-water	-	5.2%
Water-in-oil	-	41.9%
Water-glycol	34.5%	13.1%
Phosphate ester	8.9%	28.8%
Phosphate ester based	1.6%	11.0%
Other	8.2%	-
Total number of companies responding	84	123

Water-Glycols - The water-glycols fluids consist essentially of a four component system of water, glycol, a high molecular weight water-soluble polyglycol, and an additive package to impart corrosion resistance, metal passivation, anti-wear properties, lubrication, and bacteria and fungi protection to the overall mixture. The water generally accounts for 35 to 50% of the total mixture and the glycol, either ethylene or propylene glycol, is added to improve low temperature properties. Water-soluble polyglycols are added as thickeners to provide the desired viscosity for the final system. These materials are true solutions, not emulsions. Performance differences between fluids from different sources are directly related to the differences in the proprietary additive packages.

Emulsion fluids - These fluids are two-phase systems containing oil and water, and are easily recognized by their "milky" appearance. Two types of systems are available: (a) water-in-oil ("invert") emulsions; and (b) oil-in-water emulsions. Of the two classes, the oil-in-water emulsions were developed first and have been utilized for many years in the metal industries.

In the strictest sense, oil-in-water emulsions are not actually classified as hydraulic fluids. These emulsions generally consist of water and an emulsifiable fluid concentrate or "soluble oil" which contains base oils and additives in 2 to 5% concentration to impart corrosion protection and oiliness characteristics to the water. Since the basic component of this system is water, the low viscosity of this fluid does not permit its use in medium- and heavy-duty equipment.

The other types of emulsions are the water-in-oil fluids ("invert" emulsions), which are relatively recent developments in the field of hydraulic fluids. These fluids are formulations consisting of oil plus an additive package emulsified with approximately 35 to 40% water. In these emulsions, water is the dispersed phase and the oil is the continuous phase as opposed to the previous system in which water was the continuous phase. The additive package provides the normal protections against wear and rust as well as emulsifying agents and other additives.

Phosphate Ester-Oil Blends - These fluids, comprised of a mixture of phosphate ester and refined petroleum stocks, are finding increasing use as a practical approach to the need for less hazardous hydraulic fluids where the fire hazard is moderate. As currently formulated, they consist of 30 to 50% triaryl phosphate ester plus petroleum oil and a coupling agent to create solution stability. These fluids are generally available in a wide range of viscosity grades dependent upon the quantity and type of oil used in the blend. The blend normally contains additives which improve corrosion resistance and oxidation stability. The triaryl phosphate esters utilized in these blends are the same as those used in the normal phosphate ester fluids.

Phosphate Esters - These materials are often termed "synthetic" or "straight synthetic" fluids because the fluids are man-made and may possess definite chemically identifiable structures. Those companies who market the phosphate esters list the following reasons for the use of synthetics as opposed to the other types of fire resistant hydraulic fluids:

1. Excellent fire resistance properties;
2. Excellent stability;

3. Excellent lubricity;
4. Requires minimum maintenance; and
5. Can be readily reclaimed.

However, these fluids have the disadvantages of high relative cost and the need for special seals and gaskets of Viton or butyl or propyl elastomers.

The main phosphate esters used as fire retardant hydraulic fluids are tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, isopropylphenyl diphenyl phosphate, and Monsanto's proprietary, mixed alkyl aryl phosphate ester. The first three materials are the "older" types of hydraulic fluids while the latter two materials are more recent additions to the field.

Estimated consumption figures, prices, and net value for the four phosphate esters in hydraulic fluids from 1964 to 1973 are shown in the following list.

Year	Total quantity consumed ($\times 10^6$ lb)	Average price/lb	Net value (millions of dollars)
1964	10.0	$0.30	3.0
1965	13.5	$0.33	4.5
1966	15.3	$0.33	5.0
1967	16.5	$0.34	5.6
1968	17.7	$0.36	6.4
1969	19.0	$0.35	6.7
1970	20.5	$0.36	7.4
1971	22.0	$0.36	7.9
1972	29.0	$0.36	10.4
1973	37.0	$0.36	13.3

The price per pound figures are estimated average values. Several different phosphate ester fluids are available, depending upon the viscosity and additive requirements, and all are priced individually. Since the precise quantity of phosphate ester utilized in each of the several types is unknown, an average price was used.

Information from representatives of companies in the field of hydraulic fluids state, that until 3 to 4 years ago, the annual growth was approximately 5 to 10%/year and that from about 1971, the growth rate was 10 to 20%/year with the rate closer to 20 than 10%.

Earlier in this section, reference was made to two surveys conducted in the area of hydraulic fluids, one for 1964 and one for 1970. In the 1964 survey, it was found that 6.6% of the total hydraulic fluids in use were of the fire resistant type and within the fire resistant group, 8.9% were phosphate ester and 1.6% were phosphate ester-based fluids (50% ester). This leads to a total percentage of phosphate ester in use of 9.7%. In 1964, approximately 150 million gallons of hydraulic fluids were used for industrial and military purposes or a utilization of about 960,000 gal. of phosphate ester. Assuming a density of approximately 10 lb/gal, 9.6 million pounds of phosphate ester was used in hydraulic fluids in 1964. For 1970, the survey indicated that 21.8% of all hydraulic fluids were fire resistant and that phosphate esters comprised 34.3% of all the fire resistant fluids. Using the annual consumption of 197 million gallons stated by Tovey[6] and the same density values as above, the calculated total usage of phosphate esters in 1970 would be approximately 147 million pounds. The 1970 estimated figure in this study, of approximately 20 million pounds per year, is in agreement with phosphate ester manufacturers' estimates.

Process technology of phosphate esters - The processing of phosphate ester hydraulic fluids consists basically of a physical mixing operation. For formulation, the esters are pumped from storage through automatic weighing devices to a blender, proprietary additive packages added, and the components are agitated by electrical stirrers to insure complete mixing of the various components. After the mixing operation, the fluid is pumped either to storage tanks for bulk shipment by railway tankcar or truck tankwagons or to the packaging area where the fluid is placed in containers. Losses of the fluids within the formulation plants are very minimal due to the lack of physical handling of the materials throughout the entire process.

The formulated fluids are packaged in 1-qt cans (24/case), 1-gal. cans (six/case), 5-gal. cans (individually and in shrink-wrapped pallets of 24), 55-gal. steel drums (interior spray coated), truck tankwagons, and railway tankcars. Very little hydraulic fluid is shipped in the smaller containers and the vast majority is shipped either in the shrink-wrapped pallets or larger containers (drums, tankcars, etc.).

The three major formulators of phosphate ester hydraulic fluids are shown below with each of the various fluids produced by that company.

Company	Products	
	Synthetic	Ester blend
E. F. Houghton and Company	Houghto-Safe	Vital
Philadelphia, Pennsylvania	1010	23
	1055	29
	1115	5310
	1120	
	1130	
Monsanto Industrial Chemicals Company	Pydraul-E	Pydraul-C
St. Louis, Missouri	10-E	230-C
	29-E-LT	312-C
	30-E	540-C
	50-E	MC
	65-E	
	90-E	
	115-E	
Stauffer Chemicals Company	Fyrquel	Fyrtek
Gallipolis Ferry, West Virginia	90	295
	150	
	220	
	300	
	550	

These three companies are estimated to formulate over 95% of all fire resistant hydraulic fluids containing the phosphate esters being considered in this study. E. F. Houghton formulates its fluids primarily from isopropylphenyl diphenyl phosphate and trixylenyl phosphate, both of which are purchased primarily from FMC Corporation. Stauffer Chemicals Company uses primarily tricresyl phosphate and cresyl diphenyl phosphate in its formulations and Monsanto Industrial Chemicals Company formulates the majority of its fluids from their mixed aryl and alkyl aryl proprietary mixture. It is thought that Monsanto may also use some quantities of octyl diphenyl phosphate in hydraulic fluid formulations.

Other companies who formulate phosphate ester hydraulic fluids but on a much smaller scale are shown in the following list:

Company	Location
Mobil Oil Company	Edison, New Jersey
Exxon Oil Company	Bayonne and Bayway, New Jersey
Gulf Oil Company	(formulated and packaged for them by Stauffer)
Metal Working Lubricants	Detroit, Michigan
D. A. Stuart Oil Company	Chicago, Illinois
Standard Oil of California	Belle Chasse, Louisiana

Prior to about 1969, most of the phosphate ester hydraulic fluids were formulated from tricresyl phosphate with some smaller quantities of cresyl diphenyl phosphate and trixylenyl phosphate being used. Since that time, isopropylphenyl diphenyl phosphate, originally imported in small quantities by FMC from Ciba-Geigy in England, and Monsanto's proprietary mixture have gained in popularity and at the present time share the market with the "older" type materials. Industry sources indicate that, in 1973, the market for phosphate ester hydraulic fluids was approximately split equally between the "older" type esters (TCP, CDP, and trixylenyl), the isopropylphenyl diphenyl ester and the Monsanto proprietary mixture.

Phosphate ester use areas -. Phosphate ester hydraulic fluids are used primarily in industries where a significant fire hazard would exist if a rupture or leak would occur in a hydraulic line. Examples are provided below for various fields in which the fluids would be used in hydraulic systems.

* Military uses

  MIL-H-19457B (ships) for use on aircraft carriers in aircraft catapult systems, flight deck elevators, and other hydraulic systems on the flight deck.

* Industrial uses

  Die-casting equipment--other than automotive
  Steel mill equipment such as hydraulic doors on blast furnaces, continuous casting equipment, etc.
  Molding equipment--plastics industry
  Die-casting equipment and foundries--automotive industry
  Continuous casting equipment in basic metals industry
  Mobile equipment such as endloaders, bulldozers, etc., in service near sources of high temperature (e.g., endloaders used near blast furnaces in the steel industry)
  Gas turbine bearing lubricant (main bearings)
  Industrial air compressor lubricant
  Control fluids for steam turbines (electrical generation)

The automotive and steel industry use approximately 65 to 70% of all phosphate ester hydraulic fluids. Gas turbines and electrical power generation represent the fastest growing use areas.

It has been estimated that approximately 80% of the annual consumption of phosphate ester hydraulic fluids occurs due to leakages in the hydraulic system. In certain industries, the companies feel that it is more economical to continually add hydraulic fluid to the system than to shut down the system and its associated equipment, repair the leakage, refill the system, and start the system anew.

In the 1970 report by Hydraulics and Pneumatics magazine,[7] a listing of the companies responding to the survey was made by industry SIC number, the number of responding companies, and the total gallons used by those companies. In Table 5 data are shown for those companies indicating a usage of phosphate ester or phosphate ester-blend hydraulic fluids as reported in that survey.

Reprocessing - Small quantities of phosphate ester hydraulic fluids are reprocessed each year but this quantity probably represents only about 10% of the total amount of phosphate ester hydraulic fluids sold each year. Most of the reprocessing is done on a toll basis. Some of the formulating companies have an agreement with the customer to reprocess the fluid and the fee is incorporated into the selling price. The four companies shown below are the major reprocessors; however, some companies in specific industries, such as automotive and steel, reprocess their own hydraulic fluids. These quantities are not included in the 10% figure.

Company	Location
E. F. Houghton and Company	Philadelphia, Pennsylvania
Radco Corporation	St. Charles, Illinois
Findett Incorporated	St. Charles, Missouri
Wallover Oil Corporation	East Live ool, Ohio

Future growth - The use of the phosphate esters in this report in synthetic fire resistant hydraulic fluids had followed a fairly nominal growth rate until 1971. From 1971 to 1973, the growth rate increased substantially due to increased concern regarding fire hazards and recent new legislation regarding flammability. With the economic recession of 1974 and thus far in 1975, it is anticipated that the consumption of phosphate esters will decrease somewhat from the top of 1973. Provided that the economy corrects itself in 1975, it could be anticipated that the use of these

Table 5. USAGE OF PHOSPHATE ESTER HYDRAULIC FLUIDS BY INDUSTRY[3/]

SIC	Industry	Phosphate ester Plants	Phosphate ester Gallons	Phosphate ester Plants	Phosphate ester Gallons
19	Ordinance			1	100
20	Food			1	150
22,23	Textile, Apparel			1	550
28	Chemicals	4	1,400	3	3,050
29	Petroleum	1	1,500		
32	Stone, clay, and glass	3	1,135		
33	Primary metals	11	100,175	2	5,450
34	Fabricated metal products	4	2,000	1	1,000
35 Total	Machinery (except electrical)	17	18,370	12	135,269
351	Engines and turbines	3	1,200	4	128,844
352	Farm machinery and equipment	3	850	1	650
353	Construction and mining equipment	2	600	1	500
354	Metalworking machinery	1	500		
355	Special machinery, except metalworking	4	1,260	4	2,275
356	General industry machinery	2	1,300	1	500
357	Office and accounting machinery	1	660		
358	Service industry machinery			1	2,500
359	Misc. machinery (except elec.)	1	12,000		
36	Electrical machinery	3	1,500	1	200
37 total	Transportation equipment	12	1,583,475	3	501,300
371[a/]	Motor vehicles	4	1,007,000	1	500,000
372[b/]	Aircraft (missiles)	3	67,000	1	300
38	Instruments	1	150	2	10,005

a/ Includes gallonage reported as the total company usage in all plants by two automobile manufacturers. The number of manufacturing plants to which these figures apply is not known.

b/ Includes commercial aircraft, which is treated separately in this study.

phosphate esters will increase at an average annual rate of 9 to 11%. This growth rate would lead to an annual consumption of 74 to 88 million pounds in 1984. This anticipated growth rate does not imply, of course, that all phosphate esters will increase at that rate. Tricresyl phosphate and cresyl diphenyl phosphate will likely show a decreased usage in this area while the isopropylphenyl diphenyl ester will probably increase as will other proprietary mixtures. The search for new phosphate esters will continue and the introduction of new products could have a profound effect upon these projected quantities.

Aircraft Hydraulic Fluids

Aircraft hydraulic fluids have been considered separately in this report for two reasons: (a) the fluids for aircraft normally are not the same as those for industrial uses; and (b) only one of the phosphate esters considered in this study is used in formulations for aircraft hydraulic fluids, dibutyl phenyl phosphate. All other phosphate esters used in aircraft formulations are trialkyl esters. Normal phosphate ester industrial hydraulic fluids cannot be used with commercial aircraft for several reasons, the major ones of which are temperature, environment, servosystem considerations, weight, design, performance, reliability, and maintenance.

At the present time, there are two dibutyl phenyl phosphate base aircraft hydraulic fluids approved by the Federal Aviation Administration (FAA) for use in aircraft: Skydrol 500A (Monsanto) and Hijet W (Chevron). Aerosafe 2300 W is reported to contain small quantities of tricresyl phosphate to produce more desirable flow characteristics in the formulated fluid. It is likely low density (LD) Skydrol also contains some triaryl or alkyl aryl phosphate ester additives for the same reason.

Efforts to determine the quantities of dibutyl phenyl phosphate, or aircraft hydraulic fluids in general, used each year were uniformly unsuccessful. Except for rare exceptions, the Armed Forces do not use phosphate ester base hydraulic fluids in their aircraft. From discussions with a manufacturer[7] of private U.S. jet aircraft, it was determined that essentially all small private jet aircraft use the equivalent of MIL-H-5606, a hydrocarbon-base fluid, as the hydraulic fluid. Airline companies provided information regarding their usage but none for the entire industry.

The American Air Transport Association provided data on the fleet sizes of all member airlines for the years 1963, 1968, and 1972 to 1974 (see Appendix B). Similar data was obtained from the International Air Transport Association (IATA) for the years 1972 through 1974. Information

supplied by Trans World Airlines was used for the hydraulic system capacities of each type of aircraft and, from TWA, it was determined that essentially all airlines purchase sufficient quantities of hydraulic fluid for three refills of the hydraulic system per year.

Table 6 shows the calculated data for the consumption of dibutyl phenyl phosphate for the years 1964 to 1974. A density of 9 lb/gal of dibutyl phenyl phosphate was assumed. The estimated figures for all other international airlines were determined by taking the ratio between the U.S. and the international figures for 1972 to 1974 and applying this ratio to earlier U.S. consumption, as suggested by the International Air Transport Association.

It is felt that the annual consumption data in Table 6 is low, probably by 50 to 60%, but no reason for this is readily apparent.

Process Technolcgy - Aircraft hydraulic fluid are formulated in basically the same manner as that described for industrial phosphate ester hydraulic fluid. All handling and packaging procedures are the same except that aircraft hydraulic fluids are not shipped in bulk but packaged in 1 and 5 gal. containers and in 55 gal. drums. The major producer, Monsanto Industrial Chemicals Company, has been previously identified in this subsection. Chevron does not produce any dibutyl phenyl phosphate but rather purchases the fluid from Monsanto and repackages it into their containers.

Future Growth - From 1970, the use of dibutyl phenyl phosphate has increased at an annual growth rate of approximately 8%/year. During this period, the trend of passenger and freight airline was towards the large capacity planes, such as the B-747 and L-1011, which have a considerably larger hydraulic system capacity than the B-727, and others of this type. However, from recent reports, it appears that airline companies are undergoing flight consolidations, interchanging of air routes between airlines, and general changes to provide a more economical basis for the operation of the airlines. It is projected that fleet sizes will be modified to accommodate the new economy moves by the airlines and that rapid expansion of fleet sizes will not occur for the next few years. Thus, a leveling effect could occur over the next 2 to 3 years followed by a period of slower growth (approximately 5 to 7% annual growth) which would lead to a consumption of approximately 5.4 to 6.4 million pounds by 1984, based on the figures for 1974 in Table 6. If the figures in Table 6 are low by approximately 50%, as we believe, then the consumption would have been 4.5 million pounds in 1973 and 5.0 million pounds in 1974. Using these figures and an average annual growth rate of 5 to 7%, the consumption in 1984 would be in the range of 8.3 to 10 million pounds per year.

Table 6. CONSUMPTION OF DIBUTYL PHENYL PHOSPHATE IN COMMERCIAL AIRCRAFT (x 10^6 lb)

Year	United States	All other international	Total
1964	0.99	(0.59)	1.58
1965	(1.13)	(0.68)	1.81
1966	1.24	(0.74)	1.98
1967	(1.52)	(0.91)	2.43
1968	1.74	(1.04)	2.78
1969	(1.44)[a/]	(0.86)[a/]	2.30[a/]
1970	(1.55)	(0.92)	2.47
1971	(1.65)	(1.02)	2.67
1972	1.74	1.12	2.86
1973	1.83	1.23	3.06
1974	1.92	1.41	3.33

() = MRI estimate.

a/ Assumes 75% usage of dibutyl phenyl phosphate fluids from 1968 to 1974 and 100% prior to 1968.

Lubricant Additives

The area of lubricant additives is an extremely broad field, covering almost all industries where heavy or precision machinery is involved.

Phosphate ester lubricant additives can be divided into three areas: (a) extreme pressure (E.P.) agents; (b) anti-wear agents; and (c) stick-slip moderators. The first two agents or additives are used in systems involving some type of gears while the third is generally utilized in nongear situations. One also finds the term "boundary lubricant" in the literature and for the purposes of this study, boundary lubricants will be considered to be a part of extreme pressure additives.

The distinction between extreme pressure and anti-wear additives is not a clear-cut division. "Anti-wear" agent or additive is the term usually applied when reference is being made to systems operating under light to moderate loads at medium to high gear speeds. For systems operating under heavy loads at relatively slow gear speeds, the term "extreme pressure" (E.P.) additive or agent is usually applied. "Stick-slip moderator" is a new term generally applicable to additives for nongear systems. The written definitions appear to be clear-cut but in practice this is not found to be the case. A stick-slip moderator functions to reduce the lubricity, and hence slippage, while maintaining a lubricant film between the metal surfaces.

Of the phosphate esters that have been or are being used as lubricant additives, tricresyl phosphate has been the most common for many years and still is the predominant ester in this field. Small quantities of trixylenyl phosphate may be used in some applications but the extent of its usage is quite small. Among the three types of additives, anti-wear and extreme pressure additives comprise approximately 45% each and stick-slip moderators comprise the remaining 10%.

The usage of lubricant additives from 1964 to 1973, and even previous to 1964, has been marked by a rather slow, steady growth. From 1964 to about 1968, the annual growth rate was approximately 5%/year and from 1968 to present, it has progressed at a rate of about 10%/year as shown below for the years 1964 to 1973. As with hydraulic fluids, no figures could be found in the literature relative to the quantity of phosphate esters utilized during this time span; therefore, the quantities are "best estimates" based on discussions with manufacturers of phosphate esters and the annual growth rate previously discussed.

Year	Quantity of phosphate ester (x 10^6 lb)
1964	4.0
1965	4.2
1966	4.4
1967	4.6
1968	4.8
1969	5.3
1970	5.8
1971	6.4
1972	7.0
1973	7.7

Formulation Technology - The formulation of phosphate esters as lubricant additives into lubricating oils or military fluids occurs by predominately three methods. One method is that the large producers of phosphate ester hydraulic fluids (i.e., Stauffer, Houghton, and Monsanto) produce lubricating oils, containing anti-wear or extreme pressure additives, according to the specifications of a particular company or according to the military specifications. A second method of "formulation" consists of the sale of prepackaged phosphate esters, which the customer adds directly to their lubricating oil. An example of this is "Syn-O-Ad" produced by Stauffer Chemical Company. The third method involves the sale of quantities of phosphate ester to companies, such as Lubrizol, Viscosity Oils, and the major oil companies, who add the esters to lubricating oils or petroleum-based hydraulic fluids in accordance with their customer's specifications or military specifications. Examples of this latter method would be the Lubrizol Corporation, which purchases quantities of tricresyl phosphate, for incorporation (in concentrations of about 2%) into the farm tractor hydraulic and transmission fluid they produce for John Deere Company. The same procedure applies to Viscosity Oils for the fluid they formulate for International Harvester, except that in this instance the tricresyl phosphate is present in concentrations of 3 to 4%.

To assemble a listing of all users of triaryl phosphate esters as lubricant additives would be extremely complex. The situation in this use area is not akin to that in hydraulic fluids where three companies produce the vast majority of the phosphate ester fluids. With lubricant additives, a large number of companies utilize basically relatively small quantities of triaryl phosphate esters either for their own use or for the formulation of fluids according to definite specifications. For the most part, the major hydraulic fluid producers (i.e., Stauffer, Monsanto, and Houghton), Lubrizol Corporation, Viscosity Oils Company, and most major oil companies (e.g., Shell, Exxon, or Mobil) are the major consistent users of triaryl phosphate esters as lubricant additives. Other companies, who bid on military contracts for fluids containing triaryl phosphates, will employ these esters if they receive the contract but otherwise would use very little of the material.

Use Areas - Examples of current nonmilitary uses for triaryl phosphate esters in lubricants are provided in the following list. In almost all cases, tricresyl phosphate is present in concentrations of 0.5 to 2.0%, as an anti-wear or extreme pressure (E.P.) additive.

Cutting oils in metal fabrications
Machine oils (particularly for copper and brass)
Steam turbine oils
Farm machinery hydraulic and transmission fluids
Marine-type gear oils
Automotive and truck transmission fluid
Some types of shock absorbers on railway freight cars
Cooling lubricants for commercial refrigeration

The use of triaryl phosphate esters in transmission fluids serves a dual function. In addition to providing anti-wear properties, the ester also acts to maintain tight seals in the transmission.

In addition to commercial and industrial uses, the military uses appreciable quantities of tricresyl phosphate as an anti-wear additive in its fluids. A partial listing is given below of military specifications on fluids requiring the use of tricresyl phosphate as an additive.

MiL-L-7808 Main Engine Oil for Jet Aircraft (2% TCP)
MiL-L-23699 Naval Equivalent to 7808 (2% TCP)
MiL-H-5606 Hydrocarbon Hydraulic Fluid (aircraft) (2% TCP)
MiL-H-83282 Replacement Fluid for 5606
MiL-F-17111 Power Transmission Fluid (2% TCP)
MiL-L-83176 Instrument Bearing Lubricant
MiL-H-46004 Petroleum-Based Missile Hydraulic Fluid (0.5 $\pm$ 0.1% TCP)
MiL-H-27601 High Temperature, Petroleum Base Hydraulic Fluid (2% TCP)

For some of the larger volume fluids, such as 5606, 7808, 46004, and 17111, the companies listed below are examples of those usually on one or more qualified product list.

Standard Oil of California
Pennsylvania Refining Company
Royal Lubricants Company
Oronite Division, California Research Corporation
Exxon Oil Company
Bray Oil Company
Kendall Refining Company

For the military fluids shown above, the Defense Fuel Supply Center has provided figures for the quantities of each fluid purchased during

the past four fiscal years. This data, and the calculated quantity of TCP, are shown in the following list.

Fluid	Quantities purchased (gal.) FY-1974*	FY-1973	FY-1972	FY-1971
MiL-L-7808	1,051,735	838,800	2,375,050	1,362,200
MiL-L-23699	531,400	685,250	1,154,250	1,062,860
MiL-H-5606	764,660	1,908,000	2,172,500	2,480,600
MiL-H-83282	-	-	-	-
MiL-F-17111	53,050	165,100	81,000	190,250
MiL-H-27601	1,980	3,300	22,500	1,925
MiL-L-83176		No history of any purchase		
MiL-H-46004		No history of any purchase		
Quantity of TCP**	466,148	698,487	1,126,228	988,980

* FY-1974 denotes fiscal year 1974.

** Quantity of TCP (lb) calculated from percentage added according to specifications.

Future Growth - The future of triaryl phosphate esters as lubricant additives may very well find itself entering a period of slow growth or actual declining usage. At the present time, one major manufacturer has already ceased commercial sale of TCP, cresylic acid feedstock is in limited supply, and the cost of cresylic acid (and thus TCP) is increasing rapidly. If other manufacturers follow the lead of Monsanto and reduce the production of TCP in favor of the synthetic materials for hydraulic fluids, supplies of TCP could become extremely limited and expensive. At the present time, companies using TCP as an additive are searching for alternate phosphorus-containing materials as anti-wear and extreme pressure substitutes, particularly those producing fluids for farm machinery. However, current military specifications will act as a buffer to a drastic downward trend. All of the military fluids listed above specify tricresyl phosphate and the process of qualifying a new material as a substitute for TCP is somewhat lengthy.

In view of current conditions, it does not appear likely that lubricant additives, in the form of TCP, can maintain a 10% annual growth rate for an extended period of time. A leveling of the growth rate would seem appropriate for 2 to 3 years, followed by either a decline, if other companies drastically reduce production of TCP, or a period of slower growth, depending upon the decision of the other manufacturers with respect to tricresyl phosphate. The next 2 to 3 years will be rather decisive regarding the future growth of triaryl phosphate ester in this area. If the triaryl

phosphate esters can continue to participate in this area, it could be anticipated that their annual consumption in this area would reach approximately 14 million pounds per year by 1984.

FIRE RETARDANT PLASTICIZERS

General Discussion

Production of plasticizers in the United States exceeds 1.35 billion pounds per year and worldwide production is in excess of 2.3 billion pounds per year. Worldwide, there are over 500 different plasticizers. Phthalate esters constitute approximately 63% of the total production of plasticizers.[9] Between two-thirds and three-fourths of all plasticizer production, and 80% of the phthalate esters are used in flexible polyvinyls[10] with the production of poly(vinyl chloride) being more than 85% of the production of polyvinyls.[11]

Unplasticized poly(vinyl chloride) (PVC) is a rigid, flame retardant plastic, with its inherent flame retardancy due to the high chlorine level contained in the molecule. However, the majority of the uses of PVC require a flexible film which, of course, necessitates the use of a plasticizer at about 20 to 35 phr (parts per hundred parts resin). The most common plasticizer for PVC is dioctyl phthalate (DOP). The use of this plasticizer, in quantities sufficient to provide a flexible film, also "dilutes" the chlorine level of resultant plastic such that it no longer is flame retardant. Therefore, an additional plasticizer with flame retardant properties or a synergist must also be combined into the resin mixture. The addition of only a flame retardant plasticizer is also used in numerous applications. It is important to note that all monomeric plasticizers, except those containing halogens or phosphorous, increase flammability.

The rate of flame retardant resin consumption has accelerated rapidly in recent years with the increased demand being prompted by the establishment of fire safety regulations. Imparting a specified level of flame retardancy to a plastic composition, in general, can be accomplished with relative ease. However, it is considerably more difficult to develop a flame retardant plastic composition that is economical, easily processed, and provides the desired properties. Factors to be considered in formulating a new flame retardant plastic include: (a) flame retardancy; (b) physical properties; (c) processability; and (d) economics. Flame retardants, classified by functions, can be divided into three main categories: reactive, additive, and synergistic types. Reactive flame retardants contain functional groups which permit their incorporation directly into the polymer chain through chemical reaction. Additive flame retardants are incorporated into resins by compounding and one additive may be potentially useful in a variety of polymer systems. This multipurpose usefulness

is in opposition to the reactive types which are relatively specific for a given polymer system. Aryl and alkyl aryl phosphate esters are this type of flame retardant. Synergism is the phenomenon in which the combined effect of two agents working together is greater than that predicted by evaluation of the effect of each additive employed individually. A synergist is frequently used to enhance the effectiveness of the principal flame retardant. Antimony oxide is the most widely recognized example of this product class and is used primarily in combination with halogenated organics.

Triaryl phosphates, such as tricresyl phosphate and cresyl diphenyl phosphate, are among the most effective flame retardant plasticizers; in addition, they enhance the processability of polymer compositions (predominately PVC) and reduce volatility. Alkyl aryl phosphates, such as 2-ethylhexyl diphenyl phosphate and isodecyl diphenyl phosphate, offer a compromise of flame retardance and overall plasticizing properties, since some triaryl phosphates have rather poor low temperature properties. Triaryl and alkyl aryl phosphates provide self-extinguishment in flame tests when employed at a level of approximately 25% replacement of dioctyl phthalate (DOP) in a typical flexible formulation of poly(vinyl chloride). Phosphate esters do, however, have the disadvantage that they tend to increase smoke production in polymer systems.

Phosphate Esters

The principal phosphate esters that are being, or have been, used as flame retardant plasticizers in polymeric systems are:

Tricresyl phosphate (TCP)
Cresyl diphenyl phosphate (CDP)
Triphenyl phosphate
Isopropylphenyl diphenyl phosphate
2-Ethylhexyl diphenyl phosphate
Isodecyl diphenyl phosphate

Due to recent price increases for cresylic acid feedstock, the price of tricresyl phosphate has increased considerably and, as a result, has lost a portion of its market to other triaryl phosphate esters, such as cresyl-diphenyl and isopropylphenyl diphenyl. Similar cost increases are also true for cresyl diphenyl phosphate but the feedstock price increases should have a smaller impact on its price due to the lower cresylic acid content. Isopropylphenyl diphenyl phosphate, prepared from propylene, phenol, and phosphoryl chloride, is not dependent upon the supply of cresylic acid and thus is offered as a substitute for the other triaryl phosphates.

Phosphate esters are utilized as plasticizers almost exclusively for their fire retardant properties. Phosphate esters account for a rather minor fraction of all plasticizers used by the plastics industry. The overall use in the plastics industry of all of the esters listed in this subsection in 1973 was approximately 42 million pounds; by comparison, the production of the most common plasticizer, dioctyl phthalate (DOP), was approximately 430 million pounds in the same year.

The total quantity of nonhalogenated phosphate esters used as fire retardant plasticizers has increased from 34 million pounds in 1964 to approximately 70 million pounds in 1973 as shown below in data taken from the annual summaries of "Modern Plastics."

Year	Nonhalogenated phosphate esters (x 10^6 lb)
1964	34.0
1965	38.0
1966	41.0
1967	43.0
1968	47.0
1969	50.7
1970	57.0

These data provide information for all nonhalogenated phosphate esters and include data for any trialkyl esters used as plasticizers. In the 1967 "Modern Plastics" summary, it was stated that tricresyl phosphate, cresyl diphenyl phosphate, and triphenyl phosphate comprised about 85% of all nonhalogenated phosphate esters used as fire retardants and that the quantities used were 19.0, 6.0, and 9.0 million pounds, respectively, with all other esters totaling 9.0 million pounds. This same issue (1967) also stated that 10.5 million pounds of 2-ethylhexyl diphenyl phosphate was used in 1966 and estimated that 12 million pounds would be used in 1967. Information acquired from various industry sources indicates that these figures for 2-ethylhexyl diphenyl phosphate are too high and that a figure of approximately 8 million pounds for each year is more realistic. The quoted figures, at least for the years 1969 to 1974, are felt to be too high unless considerable quantities, of the order of 10 to 20 million pounds per year, of trialkyl phosphate esters are included in these figures. or if the production data from the U.S. International Trade Commission is considerably understated. From past overall usage figures, it appears unlikely that the trialkyl esters would be used in those quantities. Based on information acquired from various trade publications and phosphate ester manufacturers, the data listed below represents the MRI estimate of the total quantities used as plasticizers for the six phosphate esters listed previously in this section.

Year	Quantity (x 10^6 lb)
1964	37.1
1965	38.3
1966	41.9
1967	41.3
1968	40.0
1969	33.4
1970	41.1
1971	49.8
1972	40.7
1973	41.8

To facilitate the discussion of the utilization of the phosphate esters in the plastics industry, there are generalizations which can be applied. All of the phosphate esters used as plasticizers, except for triphenyl phosphate, have the same basic use pattern and, for the most part, are interchangeable. The alkyl aryl phosphate esters impart better low temperature properties but are not as flame retardant as the triaryl esters.

For general usage as a flame retardant plasticizer, in which flame retardant characteristics and low temperature flexibility would not be overriding factors, all of these plasticizers would function equally well and the ultimate choice would be made on economic factors, i.e., the cost per pound.

In poly(vinyl chloride), the fire retardant of choice normally is antimony oxide. However, the use of this material has been restricted by the availability of the oxide. It has been estimated that the plastics industry could have used 30 to 40% more of this synergist in 1974, since it is used in conjunction with almost all other flame retardant plasticizers.[12] The use of antimony oxide also has certain disadvantages, with the principal one being that it imparts an opaqueness to the plastic and thus cannot be utilized if a clear plastic is the desired end product. It is also undesirable if the final product requires a delicate coloration (low pigmentation). In these two areas, clear plastics and delicate coloration, aryl and alkyl aryl phosphates are the plasticizers of choice.

For the phosphate esters under consideration at this point, namely TCP, CDP, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, and isopropylphenyl diphenyl phosphate, approximately 85 to 90% of their use in the plastics industry occurs as a fire retardant plasticizer with poly(vinyl chloride) and they are used either in conjunction with dioctyl phthalate (DOP) or as a substitute for DOP, depending upon the flame retardance requirements of the end product. The remaining 10 to 15% of their

use is generally spread over other systems such as other polyvinyl films (formals and butyrals), cellulosics, and, to some extent, in thermoplastics.

In addition to their usage as a fire retardant plasticizer in plastics, these esters also find minor use in other areas related to this industry. These areas include plasticizers for synthetic rubbers (3), pigment dispersants (1.5), peroxide carriers (0.5), adhesives (1), and nonlacquer coatings (0.5). The figures in parentheses represent approximate usage, in million pounds, for each area in 1973. Additional discussions will be presented later in this subsection concerning each of these areas.

Poly(vinyl chloride) Film and Sheets - Polyvinyl film and sheeting is the largest plasticizer-consuming industry segment. In 1973, producers used more than 1 billion pounds of PVC requiring in excess of 500 million pounds of plasticizers. This represents nearly one-third of the total plasticizer sales for that year.

Poly(vinyl chloride) film is produced by basically three techniques: casting, extrusion, and calendering. The majority of the film is produced by calendering, with extrusion being next and the least amount is by casting. Blown extrusion and solution casting processes produce the thinnest films while heavier gage film is produced almost entirely by calendering. Triaryl phosphates (TCP, CDP, and isopropylphenyl diphenyl) are used as PVC resin solvents in the production of solution cast films where complete dissolution of the resin and any additive ingredients is extremely important.

The major market areas for the poly(vinyl chloride) industry and the percentage contribution of each specific area is given in Table 7 for the years 1964 to 1974. For 1973, an approximate percentage utilization of the phosphate esters within more defined use areas is given below:

Percentage	Use area
31 to 35	Automotive (vinyl upholstery, dashboard covering, etc.)
13 to 14	Wire and cable covering
14 to 16	Floor and wall coverings
14 to 16	Belting (coated fabric conveyor belts used in mines, etc.)
5 to 6	Industrial fabric coating ("Brattice" cloth in mines, etc.)
8 to 9	Other film and sheeting applications
8 to 9	Miscellaneous

Table 7. MAJOR MARKETS FOR POLY(VINYL CHLORIDE); PERCENTAGE CONTRIBUTION OF EACH MARKET AREA[a/]

Year	Building and construction	Electrical uses	Household uses	Packaging	Transportation	Consumer goods	Misc.[b/]
1964	(30.2)	(10.6)	(22.1)	(3.7)	(8.8)	(18.2)	(6.4)
1965	(30.0)	(10.8)	(21.8)	(4.0)	(8.6)	(17.8)	(7.0)
1966	29.9	11.0	21.4	4.4	8.5	17.0	7.8
1967	29.7	11.1	20.4	5.3	8.0	15.9	9.5
1968	29.4	13.3	19.5	7.1	8.7	16.5	5.4
1969	30.1	14.9	18.9	8.4	8.6	13.8	5.2
1970	33.2	14.0	16.9	9.0	7.4	14.0	5.4
1971	35.5	11.7	17.2	8.7	7.7	13.3	5.9
1972	39.7	10.3	14.5	7.9	6.1	12.1	9.5
1973	43.6	9.0	10.5	7.2	5.6	11.4	12.7
1974	41.8	7.9	11.0	7.2	5.7	11.5	14.9

( ) MRI estimate.

a/ Excludes exports.

b/ Examples of miscellaneous category include: agricultural uses (including pipe), credit cards, garden hose, laminates, medical tubing, novelties, stationary supplies, tools and hardware, and other small uses.

Examples of specific end-products using phosphate ester plasticized PVC are listed in Table 8. It should be stressed again that the choice of plasticizer may be dictated by a specific end use for the product.

In view of the rather varied applications for phosphate esters in the poly(vinyl chloride) industry and the large number of PVC processors who may use these plasticizers, it would be extremely time-consuming and outside the scope of this study to list all users over the past 10 years and all of their processing sites. It was estimated in 1972 that PVC products were produced by over 8,000 fabricators, either from purchased compounded resins or from compounded resins that the fabricators prepared themselves.[15] Obviously, not all 8,000 would use phosphate esters and delineating those who did use them would be extremely complicated. Therefore, a compilation is given in Table 9 for the major companies who are thought to use phosphate esters in the compounding of PVC resins.

Due to the nature of the compound process (physical mixing), it should be noted that these figures represent the capacity for compounding PVC resins in general without regard to a specific plasticizer. The production of phosphate ester compounded PVC resins is highly variable and subject to considerable variation in demand both for captive use and commercial sales.

Production of Compounded PVC Resins - The process by which phosphate esters, or any other plasticizers, are incorporated into the poly(vinyl chloride) resin is based upon physical mixing. Phosphate esters are normally purchased in either railway tankcar or tanktruck lots which, upon receipt at the processing facility, are pumped directly into storage tanks. When the particular ester is to be compounded with the resin, it is piped through an automatic weighing device into a closed, vented mixer. Poly(vinyl chloride) resin and other ingredients, such as heat stabilizers, pigmentation, lubricants, fillers, impact modifiers, and processing aids, are added to the mixer and the entire contents, at approximately 300°F, are stirred for a specified period of time to insure complete coating of each PVC resin particle. After mixing is complete, the compounded resin is piped directly to the bagging operation where the resin is placed in lined paper containers or is piped directly to a bulk storage container for shipment by either railway cars or tanktruck. Upon completion of the mixing operation, the mixer is cleaned and any residual resin is retained in drums and reworked into similar compounding operations at a later date. The compounded resin is now ready to be used in an extrusion or calendering operation to produce the final end product. This basic processing procedure is used by all compounders of PVC plasticized resins and has not changed appreciably over the past 10 years.

Table 8. END-USE PRODUCTS FOR PHOSPHATE ESTER COMPOUNDED PVC RESINS

End-use product	Comments
Shrink film packaging for cartons and boxes	
Vinyl automobile and truck upholstery	Very heavy usage in this area
Vinyl dashboard covering	Very heavy usage in this area
Vinyl coatings on fabric upholstery in automobiles and trucks	Very heavy usage in this area
Lightweight rainwear: "bubble" umbrellas	
Insulation facing material in construction	
Vinyl tarpaulins enclosing buildings under construction	
Pipe and conduit wrappings	
Wire and cable coatings and insulation	
Some vinyl wall coverings	
Vinyl floor covering industry	
"Brattice" cloth in mining industry	
Plastic adhesive bandages	
Plastisols for casting certain automotive parts	

Table 9. PRODUCERS OF PHOSPHATE ESTER COMPOUNDED PVC RESINS[13/]

Company	Capacity ($\times 10^6$ lb/year)[a/]
Borden, Inc. Borden Chemicals Division Illiopolis, Illinois Leominster, Massachusetts	470
B. F. Goodrich Company B. F. Goodrich Chemical Company Long Beach, California Henry, Illinois Louisville, Kentucky Avon Lake, Ohio Pedricktown, New Jersey	980
Diamond Shamrock Deer Park, Texas Delaware City, Delaware	328
Firestone Tire and Rubber Company Firestone Plastics Division Perryville, Maryland Pottstown, Pennsylvania	366
Goodyear Tire and Rubber Company Niagara Falls, New York	228
Occidental Petroleum Corporation Hooker Chemical Corporation (Ruco Division) Burlington, New Jersey	180
Stauffer Chemical Company Plastics Division Delaware City, Delaware	300
Uniroyal Rubber Company Painesville, Ohio	118

a/ These are published capacity figures and do not correspond very closely with actual plant capacities because design capacities presume continuous production of one material and no allowances are made for production shutdowns.

In the production of PVC cast films, triaryl phosphate esters are piped to a closed mixer in sufficient quantity to completely solubilize the PVC resin and any additives into a form of "gel." The liquid mixture is then pumped to a casting machine in which the heated gel is placed on a mirror-surfaced roller in a very thin film. Upon cooling, the gel "sets up" to form a very thin, highly plasticized vinyl film of normally less than 1 mil thickness. Such films exhibit good dimensional stability, clarity, and high gloss surfaces.

Cellulosics and Other Thermoplastics - Because it is a solid, the utility of triphenyl phosphate is severely restricted in areas such as poly(vinyl chloride) unless a suitable solvent can be found which would not cause interference under processing conditions. The area of thermoplastics represents the greatest utility for triphenyl phosphate although some use of this material is made in the plasticization of rubber and in adhesives. Triaryl and alkyl aryl phosphate esters have been used to a minor extent with cellulosics and certain specific applications of other thermoplastics. At one time 2-ethylhexyl diphenyl phosphate was used as a plasticizer in cellulose propionate. For triphenyl phosphate, the areas of greatest utilization are in cellulose acetate, cellulose acetate-butyrate, and modified polyphenylene oxide (Noryl) materials.

Noryl is a rather new molding and extrusion resin, having been introduced by General Electric Company in 1966. It is basically a modified polyphenylene oxide resin intended for applications not requiring the extra-high temperature resistance of normal polyphenylene oxide. Noryl is classified as an engineering thermoplastic and finds utilization in areas normally employing materials such as acrylonitrile-butadiene-styrene (ABS) resins.

The major market areas for the cellulosics industry and the percentage contribution of each specific area is given in Table 10 for the years 1964 to 1974. As in the case for the other phosphate esters with poly(vinyl chloride), triphenyl phosphate is employed as a plasticizer almost exclusively for its fire retardant properties since it is not an efficient general plasticizer for cellulose acetate and cellulose acetate-butyrate. One exception to this statement is in the formation of optical frames where triphenyl phosphate is added to the normal diethyl phthalate plasticizer to provide better flow characteristics for the melted resin. In 1973, approximately 60% (7.2 million pounds) of the annual production of triphenyl phosphate was consumed as a plasticizer for cellulose esters. In the generalized use areas listed in Table 10, specific uses would normally be limited to those applications in which the cellulosic materials are required to display fire retardant properties. Examples of specific end products for triphenyl phosphate plasticized cellulosics are as shown in the following list.

Table 10. MAJOR MARKETS FOR CELLULOSICS; PERCENTAGE CONTRIBUTION OF EACH MARKET AREA

Year	Automotive	Electrical appliances	Industrial sheeting	Optical goods	Packaging	Personal items[a/]	Toys	Tubing	Other
1964	(4)	(7)	(9)	(12)	(25)	(23)	(3)	(6)	(11)
1965	4.5	6.0	10.0	12.0	27.0	21.0	3.0	6.0	10.5
1966	(5.5)	(4.5)	(12.0)	(11.0)	(29.0)	(20.0)	(3.0)	(6.0)	(9.0)
1967	6.0	4.0	13.0	11.0	31.0	19.0	2.0	6.0	8.0
1968	9.0	4.0	13.0	7.0	31.0	20.0	2.0	6.0	8.0
1969	9.0	4.0	13.0	7.0	32.0	20.0	2.0	6.0	7.0
1970	9.0	4.0	13.0	7.0	33.0	20.0	2.0	6.0	6.0
1971	12.0	2.0	12.0	9.5	30.5	20.5	4.5	5.0	4.0
1972	11.5	2.4	11.5	10.3	27.9	21.9	4.1	6.1	4.4
1973	11.3	2.5	11.4	10.6	27.8	22.4	3.5	6.1	4.4
1974	10.6	2.5	11.6	11.0	27.9	23.1	3.3	5.6	4.4

( ) MRI estimate; all others from Modern Plastics, January issues except for 1971 (April 1972 issue).

a/ Examples of personal items include: hand tools, toothbrush handles, hairbrush handles, pens, pencils, etc.

Blister packaging
Face shields for industrial and recreational purposes
Box lids for greeting cards, stationary, etc.
Protective film in photographic albums
Microfilm jackets and holders
Hairdryer handles
Handles on small tools
Optical frames for eyeglasses and sunglasses

In the middle to late 1960's, cellulose esters were used in automobile and truck steering wheels, interior knobs and buttons, blister packaging, toothbrush handles, comb and brush sets, and toys. These markets were gradually either partially or completely replaced by other plastic materials more suitable for the end use product.

Production of Compounded Cellulosics - Unlike other common synthetic plastics, the cellulosic plastics are not manufactured by the polymerization of a monomer but rather by the chemical modification of cellulose, a natural polymer. Cellulose esters are commonly prepared by the reaction of chemical cellulose with the appropriate acid and acid anhydride with sulfuric acid normally present as a catalyst. For the production of plastic-grade cellulosics, some acid groups are removed from the product by hydrolysis. The plastic grades of cellulose acetate contain 38 to 40% acetyl, whereas the same grade of cellulose acetate-butyrate contains 26 to 39% butyryl and 12 to 15% acetyl.

In the preparation of the compounded cellulose esters, the appropriate ester is mixed with the plasticizer and other additives by physical mixing in the same general manner as with poly(vinyl chloride). The resultant mixture is heated to its softening point and blended into a homogeneous melt which is then formed into small rods or strips. The rods or strips are cut into 1/8 in. cylindrical or cubical pellets which can be extruded or solution cast into the final end use product. The pelletized esters are piped to either bulk storage containers for shipment by tankcar and tanktruck or to the bagging operation where the pellets are placed in paper containers for shipment to the numerous fabricators of cellulose esters.

The major compounders of cellulosics and their estimated capacity are:

Company	Capacity (x 10^6 lb)
Celanese Corporation Celanese Plastics Company Division Newark, New Jersey Belvidere, New Jersey Cumberland, Maryland	12
Eastman Kodak Company Eastman Chemical Products, Inc. Kingsport, Tennessee	20 to 25
Polymer Materials, Inc. Farmingdale, New York	6

In 1972, Celanese Corporation ceased production of compounded cellulosic esters. The capacity listed for Celanese is an estimate of their capacity in 1971, while the figures for Eastman Chemical Products and Polymer Materials, Inc., are estimated current capacities. There are several other small suppliers of compounded cellulosic esters but the two listed above are estimated to currently produce 80 to 90% of the total quantity. Polymer Materials, Inc., estimates that they currently supply approximately 15 to 20% of the market. If the various smaller companies supply approximately 10% of the current market, then Eastman Chemical Products would produce about 70 to 75% of all of the triphenyl phosphate compounded cellulosic esters. As in the case for poly(vinyl chloride), the figures presented above for the compounding capacities represent figures for plasticized cellulosic esters, not necessarily only triphenyl phosphate.

Noryl is the registered tradename for General Electric Company's modified polyphenylene oxide resin introduced in 1966. Compared to other more general, consumer-oriented plastics, such as PVC, polyethylene, polystyrene, and others, it is very expensive and, as an engineering thermoplastic, finds its greatest utility in close tolerance fabrications having high heat resistance requirements. Noryl is commonly plasticized with triphenyl phosphate and in 1973, approximately 40% (4.8 million pounds) of the annual production of triphenyl phosphate was consumed for this purpose.

Examples of specific uses for Noryl are given in the following list:

Small household appliances
Molded handles for hand-held hairdryers
Housings for electric blenders
Spray humidifier housing

Spray-steam iron casings
Home hair-setting kits with steam curlers
Housings for hand and desk calculators
Computer cash register housings
Rear window shelf in automobiles
Casing and some internal parts of medical instruments
Washing machine control panels and internal parts
Cabinet, base, doors of portable dishwashers
Portable clothes washer tubs
Certain internal parts in television sets
Windows in radar ovens and subway cars
Lighting fixtures requiring high impact resistance
Housing for lighting fixtures
Extruded moldings for electrical and air conditioning applications

Production of Compounded Noryl - Plasticization can occur in two ways for this material depending upon the method of fabrication of the final end product. In thermosetting the resin and plasticizer are mixed at elevated temperatures to give a homogeneous softened material which is fed directly into the thermosetting machine. For extrusion molding processes, the resin and plasticizer are mixed at elevated temperatures to give a homogeneous mixture in the same manner as that described previously for the cellulosic esters.

The sole producer for Noryl in the United States is the General Electric Company. Estimates for the annual consumption of triphenyl phosphate in this material by General Electric are given in the following list.

Year	Estimated annual consumption*
1966	(0.1)
1967	(0.1)
1968	(0.3)
1969	(0.7)
1970	(1.5)
1971	(2.5)
1972	(4)
1973	(4.8)

* Values are in million pounds per year.

Miscellaneous Use in the Plastics Industry - In addition to their use as plasticizers, some of the phosphate esters have additional minor uses in areas directly related to the plastics industry. The use of certain phosphate esters as a plasticizer in the rubber industry will also be discussed here because of its similarity to the plastics industry.

Pigment Dispersant - Minor quantities, generally less than 1.5 million pounds per year, of triaryl phosphate esters are used as a dispersing medium for color pigments. Tricresyl phosphate, cresyl diphenyl phosphate, and isopropylphenyl diphenyl phosphate are normally used for their solvent properties to provide a uniform dispersion of the pigments in various thermoplastics such as acrylonitrile-butadiene-styrene (ABS).

Peroxide Carriers - Prior to the polymerization of monomers such as vinyl chloride, the peroxide to be utilized to initiate the polymerization process is often dissolved or suspended in a liquid medium. Small amounts of tricresyl phosphate, less than 500,000 lb/year, are used to provide a high boiling medium and to protect the peroxide from possible contamination with other materials.

Adhesive - In the construction of materials such as laminates, the adhesive is often plasticized with phosphate esters when flame retardancy properties are a requirement for the end product. Cresyl diphenyl phosphate and tricresyl phosphate find some usage in this area. Isodecyl diphenyl phosphate is also used if the flame retardancy requirements can be met. In general, this area would utilize approximately 1% (1 million pounds in 1973) of the total annual production. Triphenyl phosphate finds usage in formulations for adhesives used in the binding of books, periodicals, and other similar materials.

Rubber Plasticizer - Triaryl phosphate esters, in particular tricresyl phosphate, have been used for many years as a general plasticizer in the rubber industry. Tricresyl phosphate and cresyl diphenyl phosphate have good solvating properties, good compatibility, impart fire resistance, and good oil and grease resistance. As with PVC, however, they lack low temperature properties so are somewhat restricted in their usage. Isodecyl diphenyl phosphate provides better low temperature properties but sacrifices some flame retardancy characteristics. All of the aryl and alkyl aryl phosphate esters, except triphenyl phosphate, find a varying degree of usage in vinyl nitrile synthetic rubbers. They are used both as general plasticizers and as flame retardants. Examples of use areas in vinyl nitrile rubbers are in appliance gaskets, ignition wires, cable jackets, shoe soles and sponge for insulation. Cresyl diphenyl phosphate and isodecyl diphenyl phosphate are used to provide flexibility and flame retardancy properties to styrene-butadiene rubber (SBR) used as foam carpet-backing materials.

Uses in the rubber industry have normally consumed approximately 4 to 6% of the total annual production of aryl and alkyl aryl phosphate esters. This percentage has held rather steady in this range for the past 10 years. As would be expected, the major users of the phosphate esters are the large rubber producing companies such as B. F. Goodrich, Firestone Tire and Rubber Company, Uniroyal, and others.

Future Growth - The future growth of phosphate esters as plasticizers is, of course, very highly dependent upon the future production of poly-(vinyl chloride). Should the recent OSHA standards for vinyl chloride monomer result in a sharp decrease in production, the phosphate esters will suffer the same fate, at least as plasticizers. Future legislation regarding flammability requirements could have a very positive effect upon the consumption of phosphate esters as plasticizers.

If it is assumed that the production of vinyl chloride monomer and consequently, poly(vinyl chloride) remains at a normal growth rate, the continued emphasis on flame retardancy would indicate, on the surface, increased consumption of the phosphate esters. It should be remembered that antimony oxide is the flame retardant of choice with poly(vinyl chloride) and that its growth has been hampered by the lack of supply. New halogenated flame retardants are also beginning to find usage in areas previously dominated by the phosphate esters.

From a consideration of past history and current factors affecting the usage of aryl and alkyl aryl phosphate esters as plasticizers, it is estimated that a future growth rate of 8 to 10%/year is probable but it could be greater than this if new legislation on flammability would be enacted. This average annual growth rate would indicate a usage in 1984 of 80 to 95 million pounds per year.

GASOLINE ADDITIVES

Aryl and alkyl aryl phosphate esters were utilized for preignition control in additive packages in gasoline. The preignition control properties were dependent upon the phosphorus content of the additive material. Basically three phosphate esters have been utilized in this area: tricresyl phosphate (TCP), cresyl diphenyl phosphate (CDP), and methyl diphenyl phosphate. Very small quantities of dimethyl xylyl phosphate may have been used by the Ethyl Corporation, but if so, this ester did not receive any widespread usage. By 1961, almost all of the tricresyl phosphate had been replaced by cresyl diphenyl phosphate and was no longer in use as a gasoline additive. The test properties of TCP and CDP were essentially identical and, thus, when the price of phenol dropped below that of cresylic acid, CDP became the replacement additive. Methyl diphenyl phosphate was produced only for usage as a gasoline additive. The estimated quantities of cresyl diphenyl phosphate and methyl diphenyl phosphate used during the time period 1964 to 1973 are shown in Table 11.

Table 11. ESTIMATED QUANTITIES OF PHOSPHATE ESTERS USED AS GASOLINE ADDITIVES

Year	Cresyl diphenyl phosphate	Methyl diphenyl phosphate	Total
1964	12.9	4.8	17.7
1965	(12.9)[a]	(5.8)[a]	18.7
1966	12.4	5.8	18.2
1967	11.8	5.9	17.7
1968	11.0	5.9	16.9
1969	(10.0)[a]	(6.0)[a]	16.0
1970	3.0	2.0	5.0
1971	1.5	1.0	2.5
1972	0	0	0
1973	0	0	0

[a] Data from Paul Levesque, FMC Corporation; the rest are MRI estimates.
Note: All figures represent million pounds.

During the time period 1964 to 1971, one major oil company advertised a gasoline additive package under the tradename "TCP." Discussion with a representative of this company[16] revealed that this tradename did not relate directly to the generic name for the additive but rather was used to denote that a phosphate ester (CDP) was being added to their gasoline for preignition control.

MISCELLANEOUS USE AREAS

In addition to the current and past primary use areas discussed previously, phosphate esters have been utilized in several other areas during the past 10 years; however, the volume of ester used in each of these areas is considerably smaller than for those previously described. The use areas discussed in this section include industries related to air filtration, lacquer coatings, and wood preservation. The exportation of phosphate esters will also be briefly discussed.

Air Filtration

Tricresyl phosphate is the only phosphate ester that has been used during the past 10 years in industrial air conditioning applications. TCP is used in two forms in these units: as a gel and as the liquid. One company, American Air Filter Corporation (AAF), uses approximately 60% of all TCP (gel and liquid) employed in this application and controls 100%

of the market for the liquid TCP baths. In 1973, approximately 3.5×10^6 lb of TCP was used in the air filtration industry, with American Air Filter Corporation using 2.1×10^6 lb of this total. Based on estimates by a spokesman for AAF, they sell approximately 20,000 gal. of liquid TCP nationally per year, or, at 9.7 lb/gal, 194,000 lb/year. This corresponds to approximately 9% of the total sales of TCP by AAF; the remainder, 1.9×10^6 lb, are used in the gel form. The remaining 40% of the total market for TCP in air filtration is not concentrated in a few companies but is widely spread among various companies who use relatively small quantities of the gel form.

The two processes of AAF which utilize TCP are the multiduty filter (liquid) and the glass fiber filter (gel). With the multiduty filter, a series of metal sheets are attached to a chain-operated conveyor type assembly. The screens (3 to 6 ft long and 0.5 ft wide) pass through a bath containing TCP, and are coated with a film of the liquid. These coated screens then pass in front of the air intake duct and the particulate matter in the air adheres to the screen. The screens are rotated back to the bath, dipped to remove the particulate matter, and receive a fresh film coating of liquid. The used TCP from the baths is generally not reprocessed at the present time and very likely is stored in drums for removal by a contract hauler.

Use of the gel form on glass fiber filters is basically the same type of process as used in home air conditioning except on a much larger scale. The glass fiber filters are sprayed with the TCP gel to provide a certain "tackiness" to the filter and improve the efficiency for collection of the particulate matter from the air.

The use of tricresyl phosphate as an air filter adhesive has been increasing over the past 10 years from an estimated less than 1% in 1966 to approximately 4% in 1969 to 7% in 1972. Future use of TCP in this area of application, however, will probably not be as rapid as past growth. With the overall decline in the production of tricresyl phosphate, the percentage of its use going to this application over the next 10 years, may increase at about the same, or greater, rate than in the past 10 years. An overall growth rate of 5 to 6%/year could be anticipated. If a suitable substitute could be found, this value would decrease very rapidly.

Wood Preservation

The wood treatment (preservation) industry utilized very small quantities of triaryl phosphate esters each year. It is estimated that less than 500,000 lb are used annually by this industry. The phosphate esters, probably very low grade or still bottom type materials, are mixed with creosote and pentachlorophenol for impregnation of railroad ties, posts, and other similarily treated lumber products.

Coatings (lacquers)

Tricresyl phosphate has been the principal phosphate ester used in this industry and is used primarily in acrylic lacquer automobile paints and, more recently, in nitrocellulose lacquers for furniture finishes. Annual consumption of TCP in this industry has remained almost constant at approximately 1 million pounds per year for the last 10 years.

Exportation

The exportation of aryl and/or alkyl aryl phosphate esters has not, within the past 10 years, been a significant factor in their utilization. During discussion with persons closely aligned with the phosphate ester industry, it was a consensus of opinion that less than 5% of the total production of the phosphate esters being considered in this study were exported in any 1 year and that a range of 3 to 5% was realistic.

Tricresyl phosphate and cresyl diphenyl phosphate are the principal phosphate esters exported, with the majority of these esters probably being sent to Canada, either as hydraulic fluids or to be formulated into hydraulic fluids. Isopropylphenyl diphenyl phosphate and trixylenyl phosphate may be exported in the future. Lesser quantities of tricresyl phosphate and cresyl diphenyl phosphate are also shipped to Japan, Mexico, and Europe.

Dibutyl phenyl phosphate is exported, probably already formulated as "Skydrol" aircraft hydraulic fluid, to most countries having a major airline, and future exportation should follow a rate consistant with the predicted increase in production of dibutyl phenyl phosphate.

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SECTION VIII

MATERIAL BALANCE AND ENERGY CONSUMPTION

This section will briefly discuss the total quantities of raw materials and energy required for the manufacture of those phosphate esters for which production quantities were published or estimated by MRI. The exception to this is p-chlorophenyl diphenyl phosphate which was produced in very small quantities and would have little impact on the resultant figures. Estimated total energy consumption and waste material production are also considered. In these calculations, an overall reaction yield of 88% was assumed, a figure which appears to be close to the actual production yield for both triaryl and alkyl aryl esters. The total production of all phosphate esters in this report was approximately 846.9 million pounds for the time period 1964 to 1973. Triaryl phosphate ester production was 704.6 million pounds and alkyl aryl esters were 142.3 million pounds.

RAW MATERIALS

The calculated total quantity of each of the raw materials consumed in the manufacture of these esters is shown in Figure 3 for the years of production from 1964 to 1973. Cresylic acid (cresol), phenol, and phosphoryl chloride are used in the manufacture of more than one ester and the total quantities of each of these materials consumed are shown below for the 10-year span. All other materials are used only in the production of specific esters and their total quantities can be obtained by referring to the above list.

ENERGY CONSUMPTION

The total energy consumed, as gas, steam, and electricity, in the production of these phosphate esters is given below for the years 1964 to 1973.

Year	Cresol	Phenol	$POCl_3$	Xylenol	Isopropyl phenol	2-Ethyl hexanol	Isodecyl alcohol	1-Butanol	Methanol	$AlCl_3$	$ZnCl_2$	Total
1964	38.20	28.71	36.79	-	-	3.67		0.94	0.66	0.64	0.09	109.7
1965	41.89	31.74	40.49	-	-	3.67		1.06	0.80	0.72	0.09	120.5
1966	47.00	31.32	42.60	-	-	3.26		1.18	0.80	0.76	0.09	127.0
1967	49.45	30.33	43.40	-	-	3.26		1.41	0.81	0.77	0.09	129.5
1968	51.44	29.49	43.70	-	-	2.04	0.46	1.65	0.81	0.79	0.08	130.5
1969	47.50	26.79	40.44	-	1.37	1.63	0.92	1.35	0.83	0.72	0.09	121.6
1970	42.58	28.21	40.14	3.05	2.28	1.63	1.84	1.47	0.28	0.72	0.11	122.3
1971	46.14	33.02	44.25	2.03	3.65	1.22	2.07	1.59	0.14	0.81	0.10	135.0
1972	42.46	32.12	42.13	1.02	5.48	1.22	2.30	1.71	-	0.76	0.11	129.3
1973	40.92	38.51	46.90	2.03	8.22	2.04	3.22	1.82	-	0.85	0.12	144.6
Total	447.6	310.2	420.8	8.1	21.0	23.6	10.8	14.2	5.1	7.5	1.0	1,270.0[b]

[a] Values are in million pounds.
[b] Total figures may disagree by 0.1 due to rounding.

Figure 3. Raw materials consumed[a]

Year	Steam[a/]	Gas[b/]	Electricity[c/]
1964	38.3	78.3	2.3
1965	41.5	84.4	2.5
1966	44.3	89.8	2.7
1967	45.2	91.7	2.7
1968	45.5	91.7	2.7
1969	42.3	85.3	2.5
1970	42.9	85.9	2.6
1971	47.4	93.9	2.8
1972	45.5	90.2	2.7
1973	51.0	102.1	3.1
Total	443.9	893.3	26.6

a/ Values in million pounds.
b/ Values in million cubic feet.
c/ Values in million kw-hr.

Energy consumption by type for the individual phosphate esters can be found in Section VI in the discussion of the respective esters.

WASTE MATERIAL PRODUCED

The only waste material or by-product which is usually recovered from this process is hydrogen chloride. A sludge or residue is found in the bottom of the still after distillation of the product. This still bottom consists of some undistilled product, spent catalyst in the form of the phenolate or alcoholate, perhaps some unreacted catalyst, and other ill-defined tarry residues. The residual still bottoms are collected and either incinerated by the manufacturer, landfilled, or removed from the production facility by a contract hauler. For the specific methods of disposal for individual companies, see the subsection on Environmental Management in Section V. Small quantities of waste products resulting from the phenol scrubber, caustic wash, and condenser are subjected to the waste treatment procedures employed at the various production facilities. In some instances, phenolic wastes are neutralized prior to treatment. Details concerning the specific methods of treatment may be found in the Environmental Management subsection.

The calculated annual quantities (in million pounds) of hydrogen chloride and still residue (termed sludge) are shown in the following list.

Year	HCl	Sludge	Total
1964	23.41	13.39	36.8
1965	25.81	14.65	40.5
1966	27.12	15.47	42.6
1967	27.60	15.83	43.4
1968	27.81	15.89	43.7
1969	25.81	15.01	40.9
1970	25.48	15.06	40.5
1971	28.18	16.46	44.6
1972	26.74	15.87	42.6
1973	29.71	17.81	47.5
Total	267.67	155.50	423.1

SUMMARY

The data presented thus far with respect to raw materials consumed, waste materials produced, and the production of aryl and alkyl aryl phosphate esters are summarized as shown.

Year	Raw materials ($\times 10^6$ lb)	Total product ($\times 10^6$ lb)	Waste materials ($\times 10^6$ lb)
1964	109.7	72.9	36.8
1965	120.5	80.0	40.5
1966	127.0	84.4	42.6
1967	129.5	86.1	43.4
1968	130.5	86.8	43.7
1969	121.6	80.7	40.9
1970	122.3	81.8	40.5
1971	135.0	90.4	44.6
1972	129.3	86.7	42.6
1973	144.6	97.1	47.5
Total	1,270.0	846.9	423.1

EXPOSURE TO MAN AND THE ENVIRONMENT

The aryl and alkyl aryl phosphate esters considered in this study are generally end products within themselves and do not undergo further chemical modification prior to their utilization in consumer products.

Their use as plasticizers (modifiers) and hydraulic fluids constitute the bulk of the annual consumption of these esters.

Of the 846.9 million pounds total production during the 10-year span from 1964 to 1973, 112.7 million pounds were used as gasoline additives for ignition control. This quantity of ester was obviously destroyed during the ignition process in the engine. The remaining 734.2 million pounds were used as plasticizers (406.4), hydraulic fluids (224.6), lubricant additives (54.2), and miscellaneous (49.0). The figures in parentheses are in million pounds.

The principal sources of exposure of the phosphate esters to man and the environment are mainly the waste streams from the manufacturing process and the final disposal or usage of consumer products. Some air emissions from manufacturing sites probably do occur but, to our knowledge, no specific data are available on the quantities emitted. Particulate triphenyl phosphate is likely present in the air in the vicinity of the drying and packaging operations within the manufacturing site but this exposure would be limited to a relatively small number of people.

Since all of the phosphate esters are insoluble in water and the liquids are heavier than water, they will settle out in lagoons and traps for possible recovery. However, due to their insolubility in water, phosphate esters biodegrade very slowly. When dispersed in water and biodegradation does occur, the esters exhibit a rather heavy oxygen demand on the system with typical BOD values in the range of 35,000 ppm of oxygen.

Degradation products resulting from the hydrolysis of these esters and impurities present in the finished products are perhaps of greater concern than the phosphate esters themselves. As shown in Appendix C, degradation results in the formation of the corresponding alcoholic and/or phenolic materials and inorganic phosphate. Quantities of free phenolic materials are also present in the final phosphate ester. These impurities and degradation products can be extracted into the aqueous phase. The extent of this extraction is dependent upon the degree of contact with effluent water and the degree of dilution.

Plasticizers (Modifiers)

The use of phosphate esters as plasticizers (modifiers) and in other applications directly related to the rubber and plastics industry consumed approximately 406.4 million pounds during the period 1964 to 1973. Estimated annual quantities were presented in Section IV.

There are two modes of ultimate destruction of the esters in plastics, incineration and environmental degradation by hydrolysis. Exposure of the esters to the environment occurs by migration of the plasticizer to the surface of the plastic material and then either vaporization into the atmosphere or a hydrolytic action occurring on the surface of the plastic. The diffusivity of plasticizers in plastic food containers has been estimated at 10^{-8} sq cm/sec,[1/] which is comparable with the values for many bimetal diffusion systems.

A study[2/] on the recycling and reuse of plastics has stated that annually about 90% of all household, commercial, and industrial solid wastes are landfilled; the remaining 10% are incinerated. This study also estimated the average service life of plastic products. Selected examples are shown in the following list.

Product	Estimated service life (years)	Assumed annual consumption of ester by product[a/]
Packaging	< 1	6%
Construction (film)	2	20%
Construction belting (MRI estimate)	2	10%
Apparel	4	4%
Household goods	5	4%
Toys	5	1%
Automotive	10	30%
Furniture	10	10%
Wire and cable	15	15%

a/ MRI data.

The A. D. Little report referenced a study of the lifetime of plastics buried in a dump for 5 years in which it was found that after 5 years, heavy plastic parts were intact but thin plastic film had disappeared. It was also found that, after the 5 years, the molecular weight of PVC in refuse was two-thirds of the original weight.

For purposes of calculation, the following assumptions are made: (a) 55% of all phosphate ester plasticized PVC has a service life greater than 10 years; (b) 45% of all ester plasticized PVC will have a service life less than 10 years depending upon specific product; (c) 10% of all PVC is incinerated in the year of production; (d) all products are landfilled immediately after their service life; and (e) all buried PVC film will completely degrade within 5 years with a linear degradation rate. Using these assumptions and consumption data, the following quantities (in million pounds) are calculated.

Year	Total ester consumption	Quantity incinerated	Quantity still in use after 10 years	Quantity to be exposed to environment during 10 years
1964	37.1	3.7	18.4	15.0
1965	39.3	3.9	19.5	15.9
1966	41.9	4.2	20.7	17.0
1967	41.3	4.1	20.5	16.7
1968	40.0	4.0	19.8	16.2
1969	33.4	3.3	16.6	13.5
1970	41.1	4.1	20.4	16.6
1971	49.8	5.0	24.6	20.2
1972	40.7	4.1	20.1	16.5
1973	41.8	4.2	20.7	16.9
Total	406.4	40.6	201.3	164.5

The quantity of phosphate ester incorporated into PVC, which was incinerated, was assumed to be completely destroyed. Plasticizer migration has occurred in the PVC still in use 10 years after production but the annual quantities exposed to the environment by this method are unknown. From the previous data and assumptions, the total annual quantity, in million pounds, of phosphate ester exposed to the environment from consumer products with a service life of less than 10 years is estimated in the following tabulation.

Year	Total quantity of ester	Quantity exposed to environment
1964	15.0	-
1965	15.9	0.18
1966	17.0	1.27
1967	16.7	2.47
1968	16.2	3.67
1969	13.5	5.16
1970	16.6	6.44
1971	20.2	6.65
1972	16.5	6.99
1973	16.9	7.49

These calculated values are only the contribution from esters produced from 1964 to 1973 and would represent a minimum value since the earlier years (1964 to 1968) would also have contributions from phosphate esters incorporated prior to 1964 into consumer products of less than 10 years service life. The later years would also be increased from consumer products produced prior to 1964 with a service life of greater than 10 years. These calculated figures should provide an insight into the order of magnitude of the emissions resulting from poly(vinyl chloride) and other polymeric materials.

Hydraulic Fluids and Lubricant Additives

For the purposes of this discussion, these two areas can be combined since their ultimate modes of utilization are very similar. Approximately 80% of the annual "consumption" of these fluids, especially hydraulic fluids, occurs due to leakage from the mechanical system and thus is exposed directly to the environment.

It is assumed that, prior to 1969, the quantity of hydraulic fluid reprocessed each year was negligible and that from 1969 to 1973, an increasing quantity of the annual production of hydraulic fluid is reprocessed. There is no information available which indicates that any of the lubricants or oils, in which phosphate esters are an additive, are reprocessed. The quantity of these fluids which is collected and disposed in a landfill is unknown but probably accounts for less than 20% of the total amount. Thus, like hydraulic fluids, approximately 80% of the total annual quantity is discharged into an industrial sewer or introduced, by other means, directly into the environment.

Based on these assumptions, the estimated annual distribution (million pounds) of phosphate esters entering the environment from this end use are shown in the following tabulation.

Year	Estimated total quantity	Reprocessed fluid %	Reprocessed fluid Quantity	Quantity leaked into environment	Quantity disposed in landfill
¶1964	15.6	0	0	12.5	3.1
1965	19.5	0	0	15.6	3.9
1966	21.7	0	0	17.4	4.3
1967	23.5	0	0	18.8	4.7
1968	25.3	0	0	20.2	5.1
1969	26.6	5	1.1	20.4	5.1
1970	28.8	5	1.2	22.1	5.5
1971	31.1	10	2.5	22.9	5.7
1972	38.9	10	3.2	28.6	7.1
1973	47.8	15	6.0	33.4	8.4
Total	278.8		14.0	211.9	52.9

The quantity of hydraulic fluid collected, during replacement of the fluid, is presumably placed in storage drums and disposed in a landfill. This method of disposal would delay its direct introduction into the environment. The length of time that the fluids would remain contained in the landfill before leaking from the containers is unknown and thus it is not possible to accurately gauge when these fluids would be introduced into the immediate environment of the landfill.

Emissions to the Media

For the phosphate esters incorporated as plasticizers in poly(vinyl chloride) and other polymeric material, the major source of entry into the environment would be in the soil and groundwater within the landfill area. Unknown quantities of plasticizer will, however, be emitted to the atmosphere during the service life of the polymer due to migration of the plasticizer to the polymer surface. Without specific diffusion data, it would be very difficult to estimate the quantity lost in this manner.

With hydraulic fluids and lubricant additives, an estimated 20% of the annual consumption is collected, stored, and disposed in a landfill. As with the plasticizers, the primary affected areas would be the soil and groundwater of the landfill area. For uncovered landfills, rupture of the containers would permit emissions to the atmosphere. However, since all of the phosphate esters used as hydraulic fluids and/or lubricant additives are liquids with rather high boiling points and low vapor pressures at ambient temperatures, emissions to the atmosphere by vaporization would probably be small.

The greatest factor in the "consumption" of hydraulic fluids and lubricant additives is leakage from the mechanical system. For industrial systems, the quantities lost from the mechanical system would likely be fairly well contained within the industrial plant and discharged into the sewer system. Emissions to the atmosphere of the industrial plant would also be more likely in these situations since, for hydraulic fluids, their main use is near sources of high temperature. Therefore any leakage would occur in an area considerably above ambient temperatures resulting in an increase in the vapor pressure and consequently greater vaporization into the plant atmosphere.

While the use of hydraulic fluids and phosphate ester containing lubricants in industrial plants comprises a very large percentage of the total consumption of these fluids (probably 85 to 90% based on use areas), other uses of hydraulic fluids and lubricants, containing phosphate esters as additives, can result in emissions to the soil and groundwater. Leakages from transmissions of tractors and trucks, aircraft hydraulic systems, military uses, and others, are examples of discharges to nonlocalized areas. As stated above, it is estimated that 10 to 15% of all phosphate ester hydraulic fluids and lubricants are discharged to the environment in nonlocalized areas and 85 to 90% are from localized areas, such as industrial plants. These estimates are based on the various applications of these fluids discussed earlier in Section VII.

Residence in the Environment

Triaryl and alkyl aryl phosphate esters probably degrade very slowly under environmental conditions. These esters are relatively insoluble in water (0.002 weight percent at 23°C) so that hydrolytic degradation is limited by the solubility of these materials in water. No reliable hydrolysis rate data could be found for these specific phosphate esters. However data was found[3] for tris (p-nitrophenyl) phosphate. Using the second order rate data for the hydrolysis of this compound and an assumed initial concentration of 10 ppm, a hydrolysis half-life was calculated to be approximately 1 year. Since nitro groups are known to be electron withdrawing groups, a weakening of the carbon-oxygen-phosphorus bonding would be expected. This should lead to a more rapid hydrolysis rate than might be expected for the phosphate esters included in this study. Based on the data for the p-nitrophenyl compound, a hydrolytic half-life of approximately 2 years might be more reasonable for the compounds in this study. This value would be only for hydrolytic action and does not consider any biological, photolytic, or other possible factors that would influence the rate of hydrolysis.

Impurities

Triaryl and alkyl aryl phosphate esters contain quantities of unreacted alcoholic and phenolic starting materials which may be of greater concern than the esters. Two of the major manufacturers have stated that phenolic impurities are present in the finished products at concentrations up to 3,500 ppm. Plasticizer grade phosphate esters undergo more purification than does the lubricant grade of the same ester so that the level of phenolic materials in the plasticizer grade is approximately one-third of that found in the lubricant grade. For plasticizer grades, phenolic impurity levels can range up to about 1,000 ppm while for lubricant grade, the level can be up to 3,500 ppm.

If an average phenolic impurity level of 500 ppm is assumed for the plasticizer grade, then approximately 430 lb of unreacted phenolic and/or alcoholic impurities are present per 1 million pounds of plasticizer. For an annual plasticizer production of 50 million pounds, 21,500 lb of impurity would be present. Lubricant grade esters have approximately four times the impurity level as does the plasticizer grade. Based on an assumed level of 2,000 ppm, about 1,720 lb would be present per 1 million pounds of lubricant grade ester. For an annual production of 50 million pounds, 86,000 lb of impurities would be present. The two grades combined yield about 108,000 lb per 100 million pounds of ester or an approximate concentration of 0.1%.

As hydraulic fluids and lubricants are used, the acid content (phenolic content) of the fluids increases rapidly so that at the time of replacement, the phenolic impurity content is considerably higher than for the fresh fluid. If the impurity content increased by a factor of 10 during its use, then for an annual consumption of 50 million pounds per year, the total phenolic and/or alcoholic impurity level would be approximately 860,000 lb.

Summary

Of the phosphate esters considered in this study, the tri (o-cresyl) phosphate has the greatest toxicity. However, due to its low concentration in the final product and its low solubility in water, it is very unlikely that sufficient quantities of this material could be consumed in natural food to pose a general health hazard. Isolated incidences of ingestion of tri (o-cresyl) phosphate have occurred.[47] In spite of their widespread industrial use, there have been few reports of symptoms in workers handling these esters.[47]

The contribution of phosphate to the environment from these materials is very small, in comparison to phosphates from such high volume materials as fertilizers and detergents. Being ubiquitous, phosphates derived from this source should not pose any hazard to the environment or to man.

The alcoholic and/or phenolic impurities, on the other hand, may pose a concern. Such chemicals are often responsible for taste and odor problems in drinking water. Threshold limits for detection of odors in aqueous solutions are 25 ppm for phenol and 2.5 ppb for cresol.[47] These threshold limits in food and water are sufficiently low that there would be little likelihood of sufficient quantities of contaminated food and drink being consumed to create a widespread health problem. There is no specific evidence of human cancer attributable to phenols or substituted phenols; however, some carcinogenicity to mice has been observed.

REFERENCES TO SECTION VIII

1. Piver, W. T., Environmental Health Perspectives, 4:61, June 1973.

2. Arthur D. Little, Inc., "Incentives for Recycling and Reuse of Plastics," Environmental Protection Agency, 1972, NTIS PB-214045.

3. Ketelaar, J. A. A., H. R. Gersmann, and F. Hartog, Rec. Trav. Chim., 71:1253 (1952).

4. Patty, F. A., ed., "Industrial Hygiene and Toxicology," Vol. II, John Wiley and Sons, New York, 1963, p. 1363, 1922.

SECTION IX

USE ALTERNATIVES

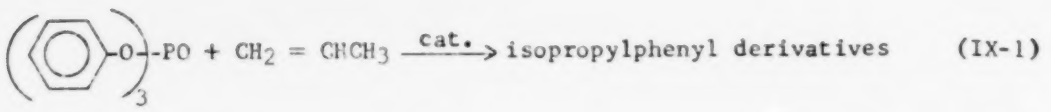
In this section, possible alternate methods of production and alternate end use materials are discussed. Topics include alternate raw materials and production processes, as well as alternate materials for the current end uses of the phosphate esters.

ALTERNATIVE RAW MATERIALS

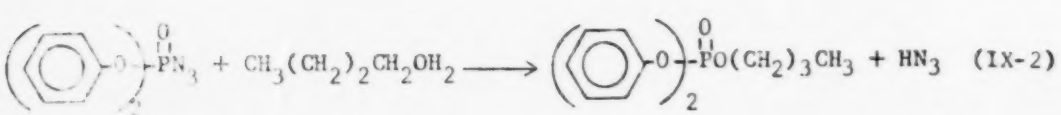
Very little work has been reported recently regarding new synthetic methods for the production of aryl or alkyl aryl phosphate esters which could utilize present production facilities. The apparent attitude is that the present process uses inexpensive raw materials; is a reasonably uncomplicated single-step reaction; and the reaction gives good overall yields.

ALTERNATIVE MANUFACTURING PROCESSES

In general, the present attitude towards new processes for these phosphate esters is approximately the same as discussed above regarding new raw materials. Two newer methods for the preparation of specific phosphate esters are shown in Eqs. IX-1[1/] and IX-2.[2/]



(IX-1)



(IX-2)

For the reaction in Eq. IX-1, the catalyst was Al_2O_3, $Al(O\emptyset)_3$, H_2SO_4, $Zr(O\emptyset)_4$, or $\underline{m}$-$(HO_3S)_2C_6H_4$. No indication was given with regard to reaction conditions, overall yield, or product distribution. The reaction of the O,O-diphenylphosphoryl azide with 1-butanol (Eq. IX-2) provides essentially a quantitive conversion to butyl diphenyl phosphate by simply refluxing the azide in a large excess of butanol for 6 hr. At the end of the reflux period, the butanol is evaporated under vacuum and the product extracted from the residue with ether. The azide is quite stable and can be distilled at 157°C at 0.17 mm without decomposition. While butyl diphenyl phosphate is not used to any significant extent commercially and was not included in this report, it is entirely possible that similar results could be obtained with other alcohols. To our knowledge, neither of the above reactions is currently practiced on an industrial scale. For Reaction IX-2, it is doubtful that the azide starting material is available in commercial quantities.

ALTERNATE FINAL USE PRODUCTS

In several use areas of aryl and alkyl aryl phosphate esters, other commercial products are available which could be used as alternates for these esters. Areas in which other products are not readily available would be as air filter media, lubricant additives, coating applications, and to a certain extent in aircraft hydraulic fluids.

For fire resistant hydraulic fluids, water-glycol and emulsion fluids could be used an an alternative in certain applications. The conversion from one fluid to another, however, is far from just draining one fluid and filling with another. Many factors must be considered in the selection of the proper hydraulic fluid. These factors include resistance to ignition and combustion, stability in service and storage, pump dynamics, chemical compatibility, bulk and vapor phase corrosion, physical properties, and cost.[3/]

In 1973, phosphate ester synthetic fluids were priced from about $3.50/gal and up; the phosphate ester based fluids were in the range of $2, to $3/gal. At the same time, water-glycol systems were priced at about 50% that of the phosphate ester fluids ($1.50 to $2.50/gal.). According to a recent article,[4/] a nonflammable hydraulic fluid priced at $0.30 to $0.50/gal. has been developed. This new fluid reportedly is compatible with standard seals and hoses, nontoxic, noncorrosive and has excellent stability. In certain instances, silicone oils may be possible alternatives to phosphate ester synthetic fluids. These oils are more expensive than the synthetic fluids ($6 to $8/gal.) and there is some question as to their fire resistance.

Each of the commonly used fire resistant hydraulic fluids require specialized disposal techniques. Emulsion type fluids must be separated by acid or certain salts into the oil and water layers. The oil layer is handled like petroleum oil and the water layer neutralized, followed by specific treatment dependent upon the contents. Water-glycol systems are completely water soluble and should be oxidized or degraded prior to discharge into a stream since they often have BOD values ranging from 50,000 to 500,000 ppm. Phosphate ester synthetic fluids are insoluble in water and heavier than water. As such, they can be settled out in lagoons or traps and reprocessed but due to the phenolic constituents present in the molecule, contact time with water should be held to a minimum to retard hydrolysis.

There are numerous commercially available fire retardant plasticizers which could be substituted for the phosphate esters. Tris(chloroalkyl) phosphate esters ($0.70 to $0.80/lb), such as the beta-chloroethyl and dichloropropyl esters, generally are compatible with about the same polymer resins as are the triaryl and alkyl aryl esters. The use of chlorinated paraffins (approximately $0.13/lb) with antimony oxide ($0.87 to $1.00/lb) could also be substituted for many of the present uses of phosphate esters. The corresponding brominated alkyl compounds (about $1.00/lb) and paraffins are also compatible with may of the plastic resins now employing triaryl and alkyl aryl phosphate esters. Zinc borates, at $0.42/lb, can be substituted in specific instances for antimony oxide. Monsanto has developed a solid phosphorus-halogen compound, Phosgard LSV, at $0.50/lb, which could replace phosphate esters in certain applications. Although many substitutes can be suggested, there are some problems to be considered. One of the major considerations must be cost of the plasticizer. Many of these suggested alternatives are more expensive than the phosphate esters and thus will increase the cost of the final consumer product. In addition, many of these possible substitutes may not provide the same degree of fire retardancy as the phosphate esters. To treat the subject of plasticizer substitutes in the most plausible manner, each specific use area should be considered with regard to economics, actual fire retardancy requirements, temperature flexibility, desired final properties of the plastic and other significant criteria. The specific criteria for each individual use varies considerably and in this manner, certain tradeoffs could be made within the use area and the best alternatives selected. A study of this nature is beyond the scope and intent of this report, however, the brief listing presented earlier could be used as a general guideline regarding the various types of materials which may serve as possible alternatives.

REFERENCES TO SECTION IX

1. Leston, G. (Koppers Company, Inc.), Ger. Offen. 2,254,399, 17 May 1974; U.S. Patent Appl. 196,728; CA, 79, p. 42146p (1973).

2. Cremylyn, R. J. W., Aust. J. Chem., 26:1,591 (1973).

3. Foitl, R. J., and W. J. Kucera, Iron and Steel Engineer, July 1964, p. 117.

4. Anonymous, Coal Age, May 1973, p. 68.

SURVEY OF INDUSTRIAL PROCESSING DATA

Midwest Research Institute is presently conducting a program for the Office of Toxic Substances of the U.S. Environmental Protection Agency under Contract No. 68-01-2687. The primary purpose of this program is to assimilate information relative to the production/formation, use and release into the environment of aryl phosphates.

The following aryl phosphates have been identified as being pertinent to this study:

tricresyl phosphate (TCP)	dibutylphenyl phosphate
triphenyl phosphate (TPP)	diphenyloctyl phosphate
cresyldiphenyl phosphate	tri-isopropylphenyl phosphate
2-ethylhexyldiphenyl phosphate	isodecyldiphenyl phosphate
mono-o-xenyldiphenyl phosphate	p-chlorophenyldiphenyl phosphate

The MRI study is based on available information in the literature and private communications with industry personnel, via telephone, letters, and questionnaire. In order to attain a statistically reliable overview of the industrial situation on the subject, it is important that we contact as many industries as possible. We, therefore, respectively solicit your cooperation in completing this questionnaire; your early response (within 4 weeks) will be sincerely appreciated.

If your department cannot supply the requested information, please forward to other departments which can respond to this questionnaire. If any questions should arise concerning this questionnaire, please contact Dr. Thomas Lapp at (816) 561-0202.

Please return the completed questionnaire to:

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110
Attn: Thomas W. Lapp

Thank you very much for your assistance and cooperation.

Pages 122 and 123 are blank.

QUESTIONNAIRE PREPARED FOR OFFICE OF TOXIC SUBSTANCES
U.S. ENVIRONMENTAL PROTECTION AGENCY

(Please fill in the details and check the appropriate blanks.)

1. Parent Corporation Name: _____

   Mailing Address: _____

   _____

   _____

2. Person to contact regarding information supplied in questionnaire.

   Dr/Mr/Ms: _____

   Address: _____

   _____

   _____

   Telephone: _____

3. If your company manufactures, or has manufactured within the past 10 years, any of the chemicals listed in the cover letter please complete the following form:

	Listed Chemical	Production Site: City or Town and State
a.	_____	_____
b.	_____	_____
c.	_____	_____
d.	_____	_____

3. Concluded.

	Listed Chemical	Production Site: City or Town and State
e.		
f.		
g.		
h.		
i.		
j.		
k.		

4. For the product(s) listed in Item 3, please state the year span during which they were manufactured and the type(s) or grade(s) produced.

	Years Produced		Type(s) or Grade(s)
	From	To	
a.			
b.			
c.			
d.			
e.			
f.			
g.			
h.			
i.			
j.			
k.			

5. Does your company export or import any of the phosphate esters?

Import: yes_____ no_____ Export: yes_____ no_____

6. If your company produces or has produced tricresyl phosphate (TCP), what is(was) the maximum limit of the ortho-isomer in the finished product?

ortho-isomer _____ %

7. What type(s) of container(s) is(are) utilized for the transportation of the finished product to the customer?

_____

_____

8 (a). Has any chemical analysis ever been made on any of your products, by-products* or process waste material to determine the presence of:

Phenols		HCl	
yes_____	no_____	yes_____	no_____

(b). If the above answer is "no", then based upon your experience, do you think that any phenols or HCl may be contained in any of your products, by-products* or process waste material?

Phenols		HCl	
yes_____	no_____	yes_____	no_____

9. Where would the phenols and/or HCl occur?

In finished product(s)? yes_____ no_____

In by-products? yes_____ no_____

In process waste materials? yes_____ no_____

* By-products are also referred to as co-products.

10. Has any chemical analysis ever been made on any of your by-products or waste material to determine the presence of the phosphate ester produced during the reaction process?

In by-products? yes_____ no_____

In process waste material? yes_____ no_____

11. For each "yes" answer to any category in Questions 9 and 10, please identify compound(s) by name(s) and form(s) (i.e., solid, liquid or gas). Also, please indicate the plant location(s) for each.*

Compound(s)	Form(s)	Plant Location(s)

*If additional space is required, please use the back of this sheet.

12. For each item listed in Question 11, please indicate the approximate concentration level of each compound(s) and where the material appears (i.e., finished product, by-product, or process waste material). If any compound appears in two or more instances, please distinguish between the entries.

Compound(s)	Concentration Level	Where Material Occurs

12. Concluded.

Compound(s)	Concentration Level	Where Material Occurs

13. To the extent possible, within the constraints of proprietary considerations, for each product identified in Item 3, please describe briefly the production process used and the approximate annual production.

Product	Process Description (e.g., major reactions carried out or U.S. Patent Number)	Approximate Annual Production (tons)

14. What waste disposal techniques do you use?

    Please describe techniques briefly and also comment on their effectiveness in preventing the release into the environment (e.g., landfill, waste pond, deep-well injection, incineration). If incineration is used, please indicate operating conditions such as temperature, retention time, gas scrubbing procedure, etc.

15. To the extent possible within the constraints of proprietary considerations, please indicate in as much detail as possible, the end uses of the aryl phosphates manufactured by your company.

16. To your knowledge, in what industry or industries would aryl phosphates occur as a manufacturing process by-product or process waste material? Any assistance you can provide in this area would be sincerely appreciated.

A discussion and summary of the replies to this written inquiry is presented in the following paragraphs.

1. Eastman Kodak Company: Eastman Kodak produces only triphenyl phosphate. The product is present as a major constituent (61%) in still bottoms (sludge) and in trace quantities in the process wash water. Phenol is present as an impurity in the finished product (0.03% maximum), in the recovered hydrogen chloride (0.002% maximum), and in the process wash water (0.63%) as well as in the sludge (0.14%). Hydrogen chloride is recovered as 35% hydrochloric acid. The liquid process wastes receive primary and secondary treatment prior to discharge into the environment. Solid waste (sludge) is incinerated at 1200°F in a three-chambered incinerator and the flue gases cleaned with a water impingement scrubber.

2. FMC Corporation: FMC produces tricresyl phosphate, cresyl diphenyl phosphate, dibutyl phenyl phosphate, and isopropylphenyl diphenyl phosphate. They produced methyl diphenyl phosphate during the period of its use in gasoline. FMC reported a 1% maximum (< 0.5% typical) concentration of ortho isomer in tricresyl phosphate. Phenolic materials occur as impurities in the finished products (300 to 1,500 ppm), recovered hydrogen chloride (1 to 200 ppm), and in process waste materials. Hydrogen chloride is recovered as 32% hydrochloric acid and is also present in process waste materials. Waste disposal treatment consists of absorption, neutralization, separation, and biological oxidation.

3. Monsanto Industrial Chemicals Company: Monsanto manufactures octyl diphenyl phosphate, dibutyl phenyl phosphate, and isodecyl diphenyl phosphate. They stated that tricresyl phosphate, cresyl diphenyl phosphate, and triphenyl phosphate production ceased in 1970. Methyl diphenyl phosphate was manufactured during its use as a gasoline additive. Small quantities of p-chlorophenyl diphenyl phosphate were produced for 2 years. Monsanto provided no information regarding quantities of waste products.

4. Sobin Chemicals, Inc.: Sobin produces tricresyl phosphate and cresyl diphenyl phosphate. They report their tricresyl phosphate contains less than 1% ortho isomer. Phenolic materials occur in the process wastewater (~ 0.02%) but not in the still bottoms. Hydrogen chloride is recovered as 20 Bé hydrochloric acid and is sold. Solid residues (still bottom or sludge) is removed by a contract hauler. Aqueous waste material is diluted and discharged into the sewer system.

5. Stauffer Chemical Company: This company manufactures tricresyl phosphate, triphenyl phosphate, cresyl diphenyl phosphate, and isopropylphenyl diphenyl phosphate. They stated that at one time, the ortho content of tricresyl phosphate was as high as 15 to 18% but is now reduced to less than 1% in all grades. Hydrogen chloride is recovered as 35% hydrochloric acid and sold. Free phenolic materials are present in both the plasticizer grade products (up to 1,000 ppm) and the lubricant grade products (up to

3,500 ppm) as well as in the effluent to the treatment system (10 to 50 ppm). Waste disposal treatment consists of degradation, carbon treatment, and landfill.

Chevron Chemical Company and Dow Chemical both stated that they did not manufacture any of the phosphate esters contained in this study. All of the companies contacted by letter responded to our inquiries.

The fleet sizes for the U.S. airlines listed below are given in Table B-1 for the 6 years in which data were available. All information regarding the number of aircraft was obtained from the Air Transport Association of America, Washington, D.C. The hydraulic system capacities for the various aircraft were supplied by Mr. George Moore, Engineer, Trans World Airlines, Kansas City, Missouri. Member airlines of the ATA are as follows:

Alaska Airlines
Allegheny Airlines
Aloha Airlines
American Airlines
Braniff International Airways
Continental Airlines
Delta Airlines
Eastern Airlines
The Flying Tiger Line
Frontier Airlines
Hawaiian Airlines
Hughes Airwest
National Airlines
North Central Airlines
Northwest Orient Airlines
Ozark Airlines
Pan American World Airways
Piedmont Airlines
Southern Airways
Texas International Airlines
Trans World Airlines
United Airlines
Western Air Lines
Wien Air Alaska
Air Canada (associate)
Canadian Pacific Air (associate)

Fleet sizes for foreign airlines were obtained from the International Air Transport Association, Montreal, Canada (Table B-2). A listing of the specific airlines included in this data would be very lengthy but the data accounts for all of the major non-U.S. airlines plus many smaller airlines. Soviet-bloc countries, such as Yugoslavia and Czechoslovakia, are included if they utilized U.S. or European-built aircraft. No Soviet Union aircraft are included in this data.

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Table B-1. U.S. AIRLINE FLEET SIZE

Type	Capacity[a/]	1974		1973		1972	
		No.	Total[b/]	No.	Total	No.	Total
B-707	35	311	32,655	315	33,075	337	35,385
B-720	35	23	2,415	44	4,620	56	5,880
B-727	35	732	76,860	710	74,550	662	69,510
B-737	35	146	15,330	134	14,070	134	14,070
B-747	176	119	62,832	109	57,552	106	55,968
DC-8	35	225	23,625	207	21,735	227	23,835
DC-9	20	389	23,340	335	20,100	329	19,740
DC-10	20	105	6,300	86	5,160	59	3,540
L-1011	136	70	28,560	48	19,584	17	6,936
Convair 880	25	--	--	37	2,775	41	3,075
Convair 990	25	--	--	--	--	--	--
BAC 1-11	20	32	1,920	43	2,580	58	3,480
Convair 580/660	18	113	6,102	129	6,066	135	4,290
Fairchild F-27	15	14	630	24	1,080	29	1,305
Fairchild F-227	15	33	1,485	31	1,395	32	1,440
L-188	25	15	1,125	19	1,425	19	1,425
L-100	25	--	--	1	75	3	225
Caravelle	20	--	--	--	--	--	--
Viscount	20	--	--	--	--	--	--
YS-11	15	21	945	23	1,035	32	990
Constellation	20	--	--	--	--	--	--
Super Constel.	25	--	--	--	--	--	--
Martin 404	10	12	360	14	420	17	510
Convair 240	10	--	--	--	--	1	30
Convair 340/440	13	--	--	6	234	7	273
DC-3	10	--	--	--	--	2	60
DC-4	10	--	--	--	--	--	--
DC-6	15	--	--	3	135	3	135
DC-7	20	--	--	--	--	--	--
CL-44	25	--	--	--	--	--	--
Others	17	12	612	42	2,142	51	2,601
Total			285,096		270,708		257,703

a/ Approximate capacity of hydraulic system in gallons.

b/ Total quantity of hydraulic fluid used; capacity x number of aircraft x 3.

Table B-1. (Concluded)

Type	Capacity[a]	1968		1966		1963	
		No.	Total[b]	No.	Total	No.	Total
B-707	35	380	39,900	212	22,260	133	13,965
B-720	35	134	14,070	126	13,230	104	10,920
B-727	35	516	54,180	223	23,415	--	--
B-737	35	66	6,930	--	--	--	--
B-747	176	--	--	--	--	--	--
DC-8	35	217	22,785	135	14,175	104	10,920
DC-9	20	260	15,600	25	1,500	--	--
DC-10	20	--	--	--	--	--	--
L-1011	136	--	--	--	--	--	--
Convair 880	25	41	3,075	47	3,525	46	3,450
Convair 990	25	6	450	17	1,275	19	1,425
BAC 1-11	20	60	3,600	38	2,280	--	--
Convair 580/660	18	148	7,992	45	2,430	--	--
Fairchild F-27	15	47	2,115	60	2,700	50	2,250
Fairchild F-227	15	55	2,475	--	--	--	--
L-188	25	86	6,450	116	8,700	117	8,775
L-100	25	9	675	--	--	--	--
Caravelle	20	20	1,200	20	1,200	20	1,200
Viscount	20	19	1,140	55	3,300	60	3,600
YS-11	15	9	405	--	--	--	--
Constellation	20	--	--	21	1,260	40	2,400
Super Constel.	25	--	--	62	4,650	111	8,325
Martin 404	10	46	1,380	77	2,310	75	2,250
Convair 240	10	3	90	44	1,320	49	1,470
Convair 340/440	13	46	1,794	138	5,382	153	5,967
DC-3	10	14	420	137	4,110	197	5,910
DC-4	10	--	--	4	120	14	420
DC-6	15	7	315	179	8,055	217	9,765
DC-7	20	15	900	54	3,240	164	9,840
CL-44	25	14	1,050	18	1,350	21	1,575
Others	17	79	4,029	115	5,865	118	6,018
Total			193,020		137,652		110,445

a/ Approximate capacity of hydraulic system in gallons.

b/ Total quantity of hydraulic fluid used; capacity x number of aircraft x 3.

Table B-2. FOREIGN AIRLINE FLEET SIZE

Type	Capacity[a/]	1974		1973		1972	
		No.	Total[b/]	No.	Total	No.	Total
B-707	35	244	25,620	230	24,150	230	24,150
B-720	35	48	5,040	39	4,095	26	2,730
B-727	35	209	21,945	184	19,320	125	13,125
B-737	35	138	14,490	104	10,920	89	9,345
B-747	176	122	64,416	94	49,632	75	39,600
DC-8	35	163	17,115	172	18,060	179	18,795
DC-9	20	261	15,660	236	14,160	210	12,600
DC-10	20	78	4,680	29	1,740	1	60
L-1011	136	6	2,448	--	--	--	--
Convair 990	25	--	--	6	450	7	525
BAC 1-11	20	55	3,300	56	3,360	50	3,000
Convair 580/660	18	4	216	4	216	4	216
Fairchild F-27	15	155	6,975	135	6,075	135	6,075
F-28	20	28	1,680	25	1,500	10	600
L-188	25	16	1,200	15	1,125	16	1,200
Vanguard	15	--	--	--	--	17	765
Caravelle	20	121	7,260	131	7,860	159	9,540
Viscount	20	30	1,800	44	2,640	57	3,420
YS-11	15	21	945	20	900	24	1,080
VC-10	35	24	2,520	34	3,570	36	3,780
HS-748	15	71	3,195	65	2,925	67	3,015
DHC-6	10	22	660	12	360	11	330
Convair 340/440	13	14	546	25	975	43	1,677
DC-3	10	57	1,710	88	2,640	127	3,810
DC-4	10	25	750	20	600	36	1.080
DC-6	15	13	585	25	1,125	43	1,935
Trident	20	69	4,140	74	4,440	70	4,200
Total			208,896		182,838		166,653

a/ Approximate capacity of hydraulic system in gallons.
b/ Total quantity of hydraulic fluid used; capacity x number of aircraft x 3.

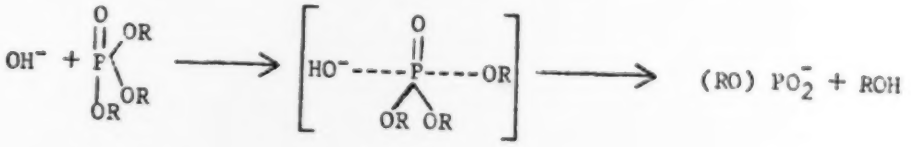
APPENDIX C

MODE OF DEGRADATION OF PHOSPHATE ESTERS

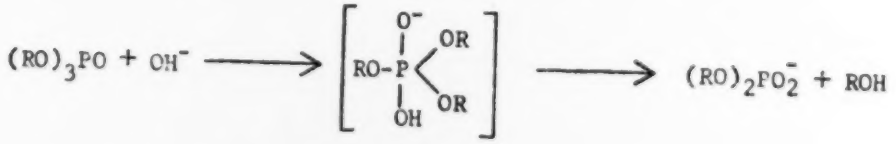
The chemical degradation of organophosphorus compounds, in general, proceeds primarily by the process of hydrolysis although oxidation or isomerization of sulfur-containing phosphorus compounds may also occur.[1/] Sulfur analogs of organophosphate esters, used primarily as insecticides, have a much more rapid hydrolysis rate than the relatively nontoxic normal phosphate esters.

Hydrolysis of phosphate esters occurs at a relatively slow rate, as stated above in comparison to the sulfur analogs, and varies in mechanism and position of bond cleavage from one class of esters to another. The most reactive of the ortho-phosphate esters are the tri-substituted esters. Hydrolysis occurs by bond cleavage predominately between the phosphorus and oxygen atoms in basic solution via an overall second-order reaction. At low pH, however, the H_2O attacks the ester grouping resulting in cleavage of the carbon to oxygen bond in a pseudo-first-order reaction. Two mechanisms have been postulated for the hydrolysis of trisubstituted esters. They are:

(1) A nucleophilic attack similar to S_N2 reactions



(2) An addition reaction followed by elimination



Most evidence supports mechanism (1); however, the two mechanisms are essentially indistinguishable if the addition and elimination process, mechanism (2), are extremely rapid.

No hydrolysis rates were given for aryl or alkyl aryl phosphate esters. Hydrolysis rates were given only for low molecular weight trialkyl esters, such as trimethyl, triethyl, etc.

1/ Griffith, E. J., A. Beeton, J. M. Spencer, and D. T. Mitchell, Environmental Phosphorus Handbook, pp. 241 and 255, John Wiley and Sons (1973).